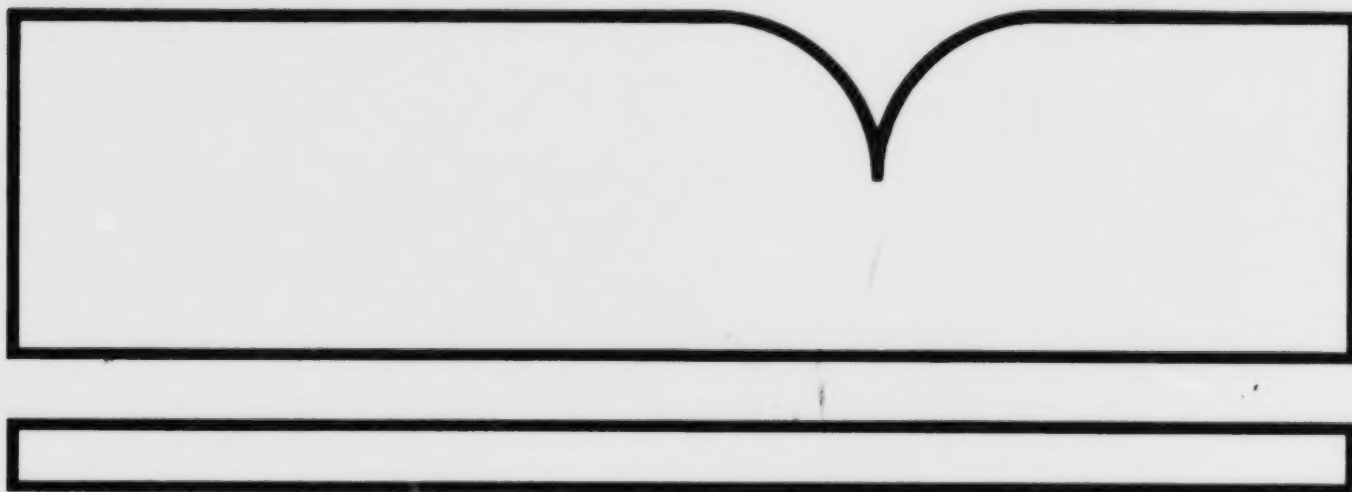


Evaluation of Foams for Mitigating Air
Pollution from Hazardous Spills

MSA Research Corp.
Evans City, PA

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EVALUATION OF FOAMS FOR MITIGATING
AIR POLLUTION FROM HAZARDOUS SPILLS

by

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research and Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

Aqueous foam blankets have become one of the prime mechanisms of vapor control with spilled hazardous chemicals. Their use has grown empirically however, and there are no guidelines for their selection or application. This report presents an evaluation of fire fighting foams as a mechanism of vapor control. It contains a use matrix, guidelines on control times and identifies the important properties of foam with respect to spill control.

Francis T. Mayo, Director
Municipal Environmental
Research Laboratory

ABSTRACT

This program has been conducted to evaluate commercially available water base foams for mitigating the vapors from hazardous chemical spills. Foam systems were evaluated in the laboratory to define those foam properties which are important in mitigating hazardous vapors. Larger scale tests were then conducted in a 3 m by 3 m pan. Polar and nonpolar liquids and liquefied gases were used as test materials.

Protein, fluoroprotein, alcohol and aqueous film forming foams were tested at low expansion ratios and surfactant foam agents at low, medium and high expansion ratios.

The chemicals tested were acetone, n-butyl acetate, di-ethyl ether, n-octane, triethylamine, benzene, toluene, ethyl benzene, cyclohexane, propane, ethylene, butadiene, ammonia, chlorine, ethylene oxide, hydrogen fluoride and sulfur trioxide. It can be concluded that all high quality foams are effective against nonpolar liquids but only alcohol foams can be recommended for polar liquids. Generalizations with liquefied gases are difficult because of their unique characteristics.

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CONTENTS

Foreword.	iii
Abstract.	iv
Figures	vi
Tables.	vii
1. INTRODUCTION	1
2. CONCLUSIONS.	3
3. RECOMMENDATIONS.	5
4. TECHNICAL DISCUSSION	6
Protein Foams.	6
Surfactant Foams	7
Fluorocarbon Surfactants	7
Modified Foams	8
Chemical Foam.	8
Foam Drainage and Collapse	9
Foam Equipment	9
Previous History of Foam Application to Chemical Spills.	11
Volatile Organic Chemical.	12
Liquified Gases.	13
Inorganic Water Reactive Chemicals	15
5. SCOPE OF WORK.	16
Task I - Delineation of Available System	16
State-of-the-Art Survey	16
Literature Search	17
Matrix Preparation.	18
Laboratory Program.	18
Matrix Revision	52
Task II - Field Testing	52
Evans City Field Tests.	54
Oklahoma Field Tests.	56
Nevada Field Tests.	61
Foam Matrix	67
Task III - Novel Foam System	67
References.	71
Bibliography.	72

FIGURES

<u>Number</u>		<u>Page</u>
1	Benzene Vapor Concentration vs Detector Height	.31
2	Benzene Vapor Concentration Percent vs Time for MSA, Lorcon, Emulsiflame.	.32
3	Benzene Vapor Concentration vs Time.	.34
4	High Expansion Foams with Nonpolar Hydrocarbons.	.35
5	Medium Expansion Foams with Nonpolar Hydrocarbons.	.36
6	Medium Expansion Foams with Nonpolar Hydrocarbons.	.37
7	Acetone with Low Expansion Foam.	.38
8	Benzene with Low Expansion Foam.	.39
9	Cyclohexane with Low Expansion Foams	.40
10	Ethyl Ether with Low Expansion Foams	.41
11	Toluene with Low Expansion Foams	.43
12	Ethyl Benzene with Low Expansion Foams	.44
13	n-Butyl Acetate with Low Expansion Foams	.45
14	Triethylamine with Low Expansion Foams	.46
15	n-Octane with Low Expansion Foams.	.47
16	Vapor Build up Over Benzene Surface Comparing Two Types of Protein Foam	.48
17	Effect of Doubling Foam A Thickness for Benzene Spill of Figure 16.	.49

18	Vapor Build up of Vapor Concentration Over Benzene Surfaces Comparing Two High Expansion Foams	.50
19	Effect of Foam Additions to Anhydrous Ammonia Spills on Downwind Vapor Concentrations	.60
20	High Expansion Foam on Liquefied Chlorine.	.62
21	Fluoroprotein Foam on Liquefied Chlorine	.63
22	AFFF on Liquefied Chlorine	.65
23	High Expansion Foam on Liquefied Chlorine.	.66
24	Ethylene Oxide Vapor Concentration During Alcohol Foam Test. .	.68

TABLES

<u>Number</u>		<u>Page</u>
1	Matrix of Foam Capabilities to Suppress or Otherwise Minimize the Release of Toxic or Flammable Vapors from Spilled Hazardous Chemicals as Listed.	.19
2	Properties of Liquefied Gases or Water Reactive Chemicals.	.22
3	Candidate Polar Materials.	.23
4	Candidate Nonpolar Materials	.23
5	Properties of Candidate Foam Agents.	.25
6	Expansion and Drainage of AFFF Foam Systems.	.26
7	Properties of High Expansion Foam Systems.	.27
8	Representative Low Expansion Foams	.28
9	Preliminary Matrix of Foam Capabilities on the Spilled Hazardous Chemicals Listed	.53
10	Foam Mitigation Times - Time for Significant Vapor Breakthrough	.55
11	Testing Sequence at Norman, Oklahoma	.57
12	Matrix for Polar and Nonpolar Liquid Hydrocarbons.	.69
13	Test Results for Novel Foam Agents	.70

METRIC CONVERSION FACTORS

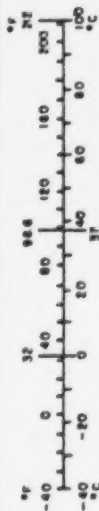
Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
LENGTH				
in	inches	2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
AREA				
m ²	square inches	6.5	square centimeters	cm ²
ft ²	square feet	0.09	square meters	m ²
yd ²	square yards	0.8	square meters	m ²
mi ²	square miles	2.6	square kilometers	km ²
	acres	0.4	hectares	ha
MASS (weight)				
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
VOLUME				
1/2 cup	teaspoons	5	milliliters	ml
1/2 cup	tablespoons	15	milliliters	ml
1/2 cup	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft ³	cubic feet	0.03	cubic meters	m ³
yd ³	cubic yards	0.76	cubic meters	m ³
TEMPERATURE (exact)				
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

* 1 cup = 240 milliliters. For other conversions, see the Metric Conversion Table, 1980, published by the U.S. Department of Commerce, Bureau of Standards, Gaithersburg, MD 20899, and the National Institute of Standards and Technology, Gaithersburg, MD 20899.

Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
LENGTH				
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
km	kilometers	1.1	miles	mi
		0.6	miles	mi
AREA				
cm ²	square centimeters	0.16	square inches	in ²
m ²	square meters	1.2	square yards	yd ²
km ²	square kilometers	0.4	square miles	mi ²
ha	hectares (10,000 m ²)	2.5	acres	ac
MASS (weight)				
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	sh
VOLUME				
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
m ³	cubic meters	0.26	gallons	gal
m ³	cubic meters	35	cubic feet	ft ³
m ³	cubic meters	1.3	cubic yards	yd ³
TEMPERATURE (exact)				
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



SECTION 1

INTRODUCTION

In the last few years significant advances have been made in the capability to control and contain spills of hazardous materials. These advances serve to minimize damage to the land and water ecosystems. These spills, however, can also provide significant air pollution and danger to life and property in the spill area. The problem is particularly acute for the personnel assigned to clean up and dispose of the spilled material.

At the time this study was initiated, water based foams had been known to be effective in controlling vapor release from some volatile chemicals. A significant body of data had been developed for hydrocarbon fuels as a result of the extensive use of foams in the control of fires of such materials. Extended tests had also been conducted with foam in the control of fires and spills of liquified natural gas. In addition to these fairly well detailed tests, restricted testing had been conducted with a number of other materials. Some results had been obtained with vinyl chloride monomer, ammonia, chlorine and sulfur trioxide.

Foam blankets act to isolate spills from ignition sources and radiant energy. Vapor release is also reduced due to the limited permeability of the foam, its capacity to absorb the chemical, or dilute the surface layer. For materials which boil below 0°C and whose gas density is less than air, foam assists in vapor dispersion by raising the temperature of the vapors as they permeate the foam layer. Water reactive chemical spills can also be mitigated by foam. They allow the gentle application of water to the surface to effect dilution and/or conversion to less hazardous chemical species without violent reaction.

Water based foams are not necessarily applicable to all volatile chemicals. In point of fact, several of the materials already mentioned require foam formulations other than those commercially available for satisfactory results. Although the reasons are not very clear, available data shows that commercially available foams are degraded by materials whose dielectric constant is greater than three.

Prior to this program the available data had indicated some potential for foam against certain classes of materials. A Coast Guard program, (Greer, 1976) which evaluated control procedures for spilled hazardous materials which float on water, had reviewed the available data. It found sound basis for

the use of foam to control the vapor hazard from spilled volatile chemicals. It found further, however, that the classes of materials to which water based foams might be applicable were not well defined.

The first task of the program was to review the state-of-the-art and evaluate the utility of foams as a means of mitigating air pollution from hazardous spills on the basis of the existing technology.

The second part was to assess the applicability of foams and foam generating equipment against individual chemicals and define the characteristics of foams which influence their compatibility and control over hazardous spills.

SECTION 2

CONCLUSIONS

The following conclusions can be drawn from the program:

1. High quality foams which have low drainage, i.e., retain their water content, performed the best in mitigating the vapors during spill control tests.
2. For nonpolar liquids, any high quality foam cover, regardless of its chemical type, will provide some degree of mitigation of vapor release.
3. Only alcohol foam was stable against highly polar low molecular weight liquids such as acetone. Other types of foam rapidly collapsed.
4. The vapors from polar spills may be mitigated with nonalcohol type low expansion foams if the volume of foam is several times greater than the volume of the spill. This reduction is mainly due to water dilution rather than a foam cover.
5. For liquids which are extremely water reactive, high expansion foam provides the best control. This is due to the heats of reaction or solution. The higher the expansion, the slower is the rate of water addition to the reactive liquid.
6. Foams do not effectively mitigate the vapors for liquefied gases which are heavier than air and not water reactive. The water draining into the liquefied gas exaggerates the boil off rate. The released vapors, being nonbuoyant, are not readily dispersed. There are reports (1) of foam being effective against butane, but the data from the tests of this program are not in agreement.
7. For liquified gases such as ethylene which are buoyant at ambient temperatures, a high expansion foam blanket acts as a heat source. The vapors rising through the foam increase in temperature and dispersion of the released vapor is enhanced.
8. For some reactive liquefied gases, such as ammonia, foam provides some mitigation of the vapor hazard due to heating of the vapor to impart buoyancy. High expansion gave the best results, attributable to a slow rate of water addition to the spill. The high expansion foam warms and scrubs the buoyant vapors as they pass through the

foam layer. Low expansion foams add water at a faster rate to the liquefied gas and large vapor clouds are produced. Foam collapse is exaggerated by reaction with the spilled material and intermittent foam makeup is required to maintain control.

9. For water reactive liquefied gases heavier than air, such as chlorine, no commercially available foam has been found to be truly effective for vapor mitigation. Although some reduction in vapor release can be achieved, reductions below 1% are difficult to realize/
10. Laboratory tests can be conducted to predict the behavior of foams under field conditions.
11. Environmental conditions such as wind and rain are more detrimental to high expansion foams than to low expansion foams.
12. High expansion foams appear to mitigate a spill by containing the vapors within the foam mass so a vapor-liquid equilibrium can be maintained, thus reducing the driving force towards vaporization.
13. Low expansion foams appear to mitigate the vapor by forming a barrier to prevent vaporization.
14. Foams are an inexpensive, effective method of initial vapor control during an accidental spill, provided the correct foam made from a quality agent is used.
15. The foam agent which produced the best results in terms of vapor mitigation was the metal stearate-based alcohol type foam. This foam agent was better than the newer forms of polar solvent foams. The alcohol type foams were more difficult to apply, more was needed to establish a desired thickness, and the foam cover is fairly stiff. However, once the foam cover was established, it provided good mitigation of vapors.

SECTION 3

RECOMMENDATIONS

The following recommendations are made for future consideration:

1. Water drainage and foam collapse rates, which are extremely important in predicting foam behavior against a spill, should be standardized both for high and low expansion foams. Drainage and collapse rate values vary greatly between manufacturers. These values can change by several hundred percent depending upon the ambient temperature and the foam generation equipment. They can also vary as a function of the drainage test employed. For low expansion foam two different techniques are listed by NFPA. For high expansion a standard test has just been incorporated into NFPA 11A.
2. Presently only alcohol type foams are recommended for polar spills. Other types of foams collapse, providing little or no protection. Alcohol foams which use a precipitation mechanism are thick and more difficult to apply. The newest polar solvent foams are more fluid but the agents are thixotropic by nature, which can be an impediment in proportioning. Alternate foam agents which are stable against polar compounds and have better flow properties would be desirable.
3. Acid or alkaline resistant high expansion foams should be developed for use on reactive liquids and liquefied gases.
5. Foams which have significantly lower drainage rates should be developed in order to be more effective against spills of liquefied gases.
6. The foam depth versus mitigation time should be examined to determine if there is a minimum or optimum thickness which must be applied to the spill in order to effectively mitigate the vapors.
7. An evaluation should be made to determine minimum application rates for foam against reactive chemicals. If the application rate is too low the spill hazard can be exaggerated to exceed the free spill hazard.

SECTION 4

TECHNICAL DISCUSSION

The application of water-based foams to the control of spills has grown out of the use of these foams for fire fighting. For the most part, foam agents and generating equipment developed for fire fighting have been used whenever foams are applied for spill control. The fact that some control could be exercised over the release of vapors from volatile chemicals tended to be incidental. Even the extensive work which has been accomplished in the last few years with LNG has used commercial foam agents and equipment. Only recently has any consideration been given to modified or novel foam systems.

Efforts to develop new foams have been made primarily because the available materials were completely unsuitable. Programs tended to become preoccupied with the development of new forms for those specific compounds which rapidly degraded standard foams. None of the programs made a systematic determination of the important characteristics of foam with respect to spill control and few determined the specific manner in which they controlled the vapor release.

Although much still remains to be done to define the full capability of foams along with their limitations, the prior work has established foam as an effective control measure. The work with LNG has begun to point out important properties of foam for cryogenics and a Coast Guard program (Greer, 1976) provided similar data for materials which float. With knowledge of how foams act with a broad range of chemicals, a base has begun to be established for modifications and improvements.

FOAM CHEMICALS

Two basic foam types are currently available -- protein-derived materials and surfactant or detergent based concentrates. A number of novel foams are available but all are modifications of a hydrocarbon surfactant system. Another foam material termed chemical foam exists, but it has ceased to be available, displaced by protein foam.

Protein Foams

Foam concentrates derived from hydrolyzed protein are widely used in the control of hydrocarbon fuel fires. Protein foams were probably the first used in spill control. In their use with fuel fires it was realized that they effectively blanketed the spill preventing the release of vapors. This characteristic has been written into specifications by both the federal government and independent laboratories. These specifications require foams

to provide a barrier to ignition for a minimum period of fifteen minutes.

Fluoroprotein foam agents are a protein base material to which fluorinated surfactants have been added to improve properties such as fluidity and surface tension, while reducing the tendency of the protein base to pick up (absorb) hydrocarbon liquids.

In addition to hydrocarbon fuels, protein based systems have been developed which are applicable to fire control of polar compounds. Marketed as "alcohol foams" they are of two types. The early systems used a metal stearate to form a protective precipitate. Newer, universal or polar solvent foams use a polysaccharide to gel the foam on contact with the polar solvent.

Although protein foam has a demonstrated capability in spill control for hydrocarbon fuels, the extent of its capability, permeation rate, fuel absorption, etc., has not been adequately defined for spill control other than with hydrocarbon fuels. Compatibility of foam with a chemical is not necessarily a measure of its ability to restrict vapor release.

Protein foams are limited to low expansion systems and the concentrates have a limited shelf life, varying with the manufacturer. They tend to be messy, difficult to clean up, and odiferous but they are usually standard items with the fire services. For that reason alone, their capabilities and limitations for spill control of volatile hazardous chemicals need to be delineated.

Surfactant Foams

Detergent foam concentrates are probably the widest used. They avoid the problems of other agents. They are suitable for both low and high expansion and most have an unlimited shelf life if stored correctly. They are not as well regulated as protein materials and as a consequence there is a wide variety of surfactant foam concentrates on the market. They represent a broad range of properties and with the lack of standards the selection of high quality foam agents can be difficult.

Current commercially available surfactant foams for fire fighting are predominantly anionic. These materials are readily available, relatively inexpensive, nontoxic and biodegradable. The amphoterics tend to be more expensive and the foaming qualities of the cationics legislate against their use. There are nonionic agents available. Nonionics have a greater tolerance for pH variations, but they are not adaptable to modification which minimizes water drainage from the foam.

Fluorocarbon Surfactants

These materials, termed aqueous film forming foams, are hydrocarbon surfactants modified with fluorocarbon surfactants to achieve a low surface tension. These materials do form aqueous foams, both at high and low expansion ratios, but the foams have very high collapse rates. In many applications, the foam is a means of applying water rather than an end in itself.

The fluorocarbon surfactants lower the surface tension of water significantly. This makes it possible to float water films on the surface of the hydrocarbon fuels. In some cases the balance is precarious and the water must be added gently to achieve floatation. Foam is used to achieve this gentle application. The basic method of fire control is thus the surface film.

The resistance to permeation of a thin film is small. Several reports have been published on vapor permeation through the surface films (Hederstand, 1924; Meldrum, 1972; White, 1976).

Modified Foams

This terminology covers recent developments but relates only to those materials which are considered commercially available.

Almost all advances have been with surfactant base materials. The basic improvement in surfactant type fire fighting foams has been with drainage and collapse rates. This has been accomplished primarily by the addition of water soluble polymeric materials to the concentrate. There are numerous literature and patent references to polymer modified foam concentrate. There are numerous literature and patent references to polymer modified foam concentrates but few materials have reached commercial availability. MSAR has used this approach in the evolution of its Type V foam which has been shown to have superior properties in fire and spill control, being the only hydrocarbon surfactant foam to pass the fire tests for both low expansion and high expansion foams specified by Underwriters Laboratory. Other complex foam agents are commercially available, which apparently use polymer additions. National Foam has a foam agent termed "Universal" which is compatible with a broad range of chemicals and more recently has started marketing a new polar solvent agent. MSAR also has a foam agent called Type L which yields a long lasting, slow collapsing foam. It, too, is compatible with a large number of material classes and has application to spill control. The 3M Company markets a Light Water Alcohol Type concentrate. This foam agent has also been advocated for spill control.

Chemical Foam

Although this kind of material is no longer available, the fact that at one time it was a major commercial product and could easily be produced justifies discussion in this section. Chemical foam was made by blending sodium bicarbonate and aluminum sulfate in water. Other chemicals are added to assist foam formation, with the foaming action provided by the release of CO₂ by chemical reaction. Sulfuric acid or similar chemicals were substituted for aluminum sulfate in special systems such as hand extinguishers.

The advent of protein foam, pressurized extinguishers and other improvements led to the demise of chemical foam as a viable system. Since chemical foams are no longer commercially available, this type of foam agent was not examined in the program.

Foam Drainage and Collapse

Although the requirements for spill control may differ from fire, water drainage is still expected to be the most significant property of a foam. It controls fluidity, resistance to thermal effects, ability to assimilate foreign materials and linear collapse rate. The slower the drainage the better is each of these characteristics. Foam agents range from simple water solutions to complex blends of components to achieve the desired characteristics. With anionic base materials, drainage can be controlled through chemical modification. As a result, commercial materials cover a range of drainages. The worst may lose 70% of their water within two minutes after generation. The best have quarter drainage times (time to drain 25% of the initial water) of 12 to 15 minutes.

Anionics exhibit a temperature transition property where the drainage changes from slow to fast over a narrow temperature range. For most this temperature is below ambient and thus they are fast draining. A few agents have transition temperatures above ambient and thus have inherently slow drainage. The best foam systems have transition temperatures in the range 29 to 35°C.

Linear collapse rates of foams are often quoted but they can be misleading. As a foam drains it leaves a dry skeleton which has little integrity. Thus the recession of effective foam thickness can be greater than the measurable collapse rate. Collapse data are significant only for slow draining foams where the dried layer may be only two to three bubble layers thicker than the effective foam thickness.

FOAM EQUIPMENT

Equipment to generate foam has been tailored to the needs of the fire service even more than the foam chemicals. Two basic categories of generation equipment exist commercially; that which yields low expansion foam generally in the range 3:1 to 12:1, and that which yields high expansion foam 120:1 to 1500:1. In this latter category, foams of less than 400:1 are now being referred to as medium expansion foam. Expansions above 1000:1 are now considered ineffective and the limited work with spills would indicate this should be reduced to 750:1.

The absence of equipment to fill the gap between 12:1 and 120:1 reflects the almost exclusive application to fires. High expansion foams have been primarily directed to three dimensional fires where total flooding of the fire area can be accomplished. High expansion foams cannot be projected very far and are affected by winds above 10 mph. Although they make less effective use of water than high expansion, low expansion foams can be projected considerable distances, are effective in open areas, and where structural cooling or coverage of vertical surfaces is required. There are no data available which show advantage in fire control for an intermediate range foam.

Other applications have been investigated where both foam stability and water conservation were important. These have been primarily agricultural applications or for cellular concrete. For this purpose a mechanical foam pump was developed which could provide expansions up to 30:1 but the equipment has not been widely used.

Both low and high expansion equipment comes in fixed and portable units. Low expansion generators come in several forms -- playpipes, applicators, air nozzles, etc. In each, the basic mechanism is the same -- air is mechanically entrained into a foam solution by agitation within a nozzle system. Unit sizes range from as low as 5 gallons to 4000 gallons per minute. The larger equipment is for fixed systems but the lower end of the range can be used in truck mounted turrets or other similar mobile installations. The largest sizes are primarily marine monitors for shipboard use. In each type of system, output and foam projection are a function of water flow and pressure. There is an optimum range of each for each piece of equipment, but foam expansion does not vary appreciably over the total range. The critical factor is to match foam agent input to water flow so that an acceptable foam is made.

High expansion foam is made by spraying a foam solution against a screen while applying blowing air from behind the screen. Foam generators range in size from 100 cfm to 55,000 cfm output. The smaller sizes are usually the air aspirating type of generator. In this form there are no moving parts. The foam solution is forced at high pressure against the foam screen. The force of the water spray aspirates sufficient air to form foam. Since air aspiration is an inefficient process, expansion ratios are by nature on the low end of the range. Small units start near 100:1 but even the larger, 1000 cfm, units do not exceed 450:1.

To achieve higher output and expansion ratios, it is necessary to incorporate a fan to provide air flow. Four types of fan drives are available -- water motor, electric motor, gasoline engine, or air motor. For reasons of reliability and safety, water driven units are beginning to predominate. Two drives are employed, one a water turbine and the second a reaction motor. The latter is lighter, more efficient but by its design the water used to drive the motor is not effectively converted into foam and it drains from the generator as a heavy froth. This has been found to be unacceptable in spill control for cryogenic or water reactive chemicals since it adversely aggravates the spill.

The small air aspirating units can produce up to 1000 cfm of foam and can be run from a hose line as portable equipment. Water and gasoline driven fan units are also available as portable or wheeled units operating off hose lines at outputs up to 6000 cfm. A few fire trucks have been built with 12,000 cfm water driven units mounted integrally. Water pressures from 40 to 80 psi are required, with the higher pressures needed for water driven units.

Foam pumps utilize mechanical agitation to make foam. Unlike low expansion units where the force of water flowing through an agitator is the foaming mechanism, the foam pump uses a motor driven agitator. It is this whipping action which provides for the expansion in the 30:1 range. The need for

the motor drive makes it possible to project the generated foam considerable distances as a foam stream.

Generators of this type have been truck mounted and driven from its power. They are utilized in the field for the generation of foam for use in cellular concrete. Other units have been tractor mounted to generate foam for agricultural application.

One additional form of foam generator deserves mention. This is the so-called flooded plate generator. In this form a perforated metal plate is mounted midway in a rectangular enclosure. The plate surface is channeled and foam solution flowed down the channels. Air is introduced underneath the plate to generate the foam. Output and expansion are controlled by the size and distribution of the perforations, the rate of solution flow and the air flow into the generator.

Flooded plate generators have application in that they are able to produce foam in the range of 100 to 200:1 with solutions too viscous to be suitable for normal high expansion generators. Thus, medium expansion foams can be made from solutions containing high percentages of water soluble polymers. These result in highly stable slow collapsing, slow draining foams. The flooded plate can also be used where high percentages of solids have been slurried into the solution. This makes it an interesting device for consideration in the application of such materials for spill control.

PREVIOUS HISTORY OF FOAM APPLICATION TO CHEMICAL SPILLS

As stated earlier, the first use of foam in spill control was with hydrocarbon fuels. Since that time there have been numerous investigations and trials with foams for control of spills of a variety of chemicals. Except for the extended work with liquefied natural gas these efforts have not been comprehensive. A significant amount of data has been generated but has never been consolidated. The Coast Guard program on hazardous chemicals that float has brought most of this data together.

The data which has been gathered shows that commercial foams can provide a variety of benefits in the control of hazardous chemical spills. These benefits fall into two categories -- the control of vapor release from the spill surface and the isolation of the flammable materials from accidental ignition. The control of vapor release is manifested in several ways. An integral foam blanket isolates the surface from radiant energy, it acts as a barrier to vapor passage and it can absorb the vapor to some extent. With cryogenics whose vapor is buoyant at ambient, the foam acts to warm the vapor such that it disperses better after permeating through the foam layer. With aggressive water reactive chemicals, foam offers a mechanism to gently add water to dilute the spill.

It should be noted that foam has not been found to be applicable to all materials or classes of materials, nor does simple foam compatibility with a chemical indicate any measure of spill control. Background knowledge in foam applicability for spill control is detailed in the following sections.

It should be recognized that foams are applicable to contained spills. They do not seem to be adaptable to running spills. Ground conditions appear to have a minimal effect on the vaporization of spilled liquids. Wet conditions can aggravate the initial boil off but it should be a transient condition. The only significant consideration comes when the spill, although contained, is absorbed or submerged in sand, gravel or similar material. Since foam can seal against such surfaces and the point of concern is vapor release, even this set of conditions was not a significant concern. On this basis it was not felt necessary to modify the laboratory tests to compensate for topographical conditions.

Volatile Organic Chemical

The largest group of materials in the hazardous chemicals list, to which foam is applicable, are the volatile organics. With this group foam has two actions -- suppression of vapor release and surface isolation. The data on the applicability of commercially available fire fighting foams to these materials has provided further substantiation of an observation made by MSAR in an earlier EPA program (Friel, 1973). These foams show compatibility only with those materials whose dielectric constant is less than three. There is no satisfactory explanation of the influence of the dielectric constant but the data is fairly conclusive.

By excluding materials above a value of three, polar compounds are excluded as are most organics with significant water solubilities. For those nonpolar chemicals which do not degrade the common foams, the data shows that the capability to restrict vapor release is a function of the solubility of the chemical, and its vapor pressure. Previous attempts to quantify these properties were not successful. An order of merit has been established and it was believed that molecular size was the most important consideration, followed by water solubility and vapor pressure. What the order of magnitude of difference may be was not clear. The molecular size feature was complicated somewhat by molecular structure, saturated, unsaturated, or cyclic and the arrangement of radical groups.

Those materials with low molecular weights, benzene and ethyl acetate for instance, have a fairly rapid permeation through surfactant foams regardless of expansion. At the other extreme large molecular sizes, such as isooctane, show extremely slow permeations and complete suppression may be observed for more than a day. In general, foams offer some measure of vapor suppression for all materials with which they are compatible where the vapor hazard is fire or explosion.

In the case of toxic materials, however, the allowable vapor concentrations are so low that foam can restrict it to less than the TLV for only very short times. By restricting vapor release it does help the downwind hazard. Workers in the area would have to use respiratory protection regardless. Restricting the vapor concentration, even though it is not below the TLV or even the minimum lethal dose, extends the life of canister protection and minimizes the hazard due to mask or hose failures.

There are at present a large number of foam agents available on the market. In absolute terms they should all provide equal protection. The bubble walls are the principal barrier and these are basically water. The small amount of surfactant does not have a significant influence. The difference comes in maintaining a specific foam thickness coupled with a slow drainage. Low drainage, low collapse foams present a superior barrier and require less makeup.

In earlier EPA sponsored work, (Friel, 1973) it was theorized that the degrading action of chemicals such as the polar compounds was due to exag-geration of drainage and/or precipitation of the surfactant. To combat this gellation was proposed as a preventive action. A pectin fortified foam was evolved which did extend compatibility to a broader range of chemicals along with a capability to control vapor release. The system, however, was not adaptable to available foam generating equipment and as yet that situation has not changed.

In more recent work universal foams have been developed and marketed with compatability with a wide range of materials. They have not show a substan-tial improvement in vapor control, however, over that possible with high quality fire fighting foams. A foam system developed as a long lasting foam for a nuclear application (Mecca, 1971) has demonstrated extended compati-bility. This foam derives its life or collapse rate from the concentration used. As the concentration was increased to extend life, the ability to restrict vapor permeation also increased. It became clear that the foam was demonstrating a capacity to absorb as well as block chemical vapors.

The mechanism of vapor passage through foam is one of slow permeation of vapor through the bubble walls. Gas concentrations in the foam bubbles can ultimately exceed the lower explosive limit. Thus, the foam could be ig-nited. High expansion foam is more susceptible to this possibility than low expansion.

If ignition does occur the burn back rate will be lower than over an un-covered surface. Should the vapor concentration be in the explosive range, the foam structure suppresses flame propagation and only burn back will occur.

Liquefied Gases

Studies have been made with a number of cryogenic materials. They show that the vapor hazard associated with spills of these materials could be mitigated by foam application.

Liquefied Natural Gas--

Of the liquified gases which have been studied, liquefied natural gas has received the majority of the attention. In worked sponsored by the American Gas Association extensive testing was carried out with commercial high expan-sion foams and equipment. The results have been quite positive.

The AGA sponsored work showed that foam aided both vapor dispersion and fire control. At the boiling point of liquefied natural gas, -161°C , the released vapor is very cold and denser than air. It moves downwind at or near ground level where it could intersect an ignition source. Tests have shown that if the vapors are forced to pass through a foam blanket a foot or more thick, they warm sufficiently to be buoyant upon release to the atmosphere. The water draining from the foam into the LNG exaggerates the boil off rate. The boil off rate is not too critical as long as the gas is warmed sufficiently to be buoyant, and the effectiveness of the foam blanket is maintained. Fast draining foams lose their fluidity and form openings in the foam layer through which the vapors can pass rapidly with a minimum of warming. Thus low draining, slow collapsing foams are desired.

These characteristics become much more important when fire is considered. Foam is not able to extinguish LNG fires; the boiling action prevents sealing of the surface. Due to the extremely low boiling point of LNG, spills rapidly freeze the spill substrate. This acts as an insulating barrier and long term thermal energy input is mainly from radiation. In a fire, foam acts as a barrier to radiant energy including reradiation from the fire. By means of energy blockage, and reductions in fire intensity as high as 95% can be achieved. Maintenance of fire control allows the spill to be burned off under controlled conditions.

Data on LNG fire control is sufficiently well developed that NFPA 11A now provides guidelines for high expansion foam system design for LNG facilities.

Liquefied Petroleum Gas--

Liquefied petroleum gas is similar in some respects to LNG. Fire control can be exercised by a foam blanket. The benefit of foam to the vapor hazard of LNG with foam is strongly influenced by the fact that the vapor can be made buoyant. This is not true for LPG, whose vapor is heavier than air at all temperatures. The question of vapor mitigation with foam for propane is still under discussion and needs further investigation.

Vinyl Chloride Monomer--

In the case of vinyl chloride monomer, there can be benefits from using foam for vapor control. In tests with VCM, no measurements were made of vapor dispersion per se. The measurements taken were of boil off rate, and significant reductions were observed. Due to its much higher boiling point, -14°C , the influence of drainage is considerably less than with LNG. Further, the VCM gas density is greater than air. As a consequence the vapor rises through a foam mass at a slow rate. It was concluded that each of these, plus the blockage of radiant energy, contributes to the reduced boil off rate.

Ammonia--

Due to the exceptionally large heat of solution, treatment of ammonia spills with water sprays is not practical even though ammonia is infinitely soluble. The early investigations with standard foams were not encouraging. Foams were rapidly degraded. Some success was realized by incorporating

materials into the foam which caused it to gel when neutralized. A system was evolved in which the foam generated gelled upon application to ammonia. Low expansion foam blankets were developed in laboratory tests which controlled vapor releases from ammonia for hours.

Attempts to utilize this system on a larger scale were unsuccessful, however. Ammonia vapor in the air caused gelling of the foam at the point of generation and plugging of the generator. Foam could be generated at some distance from the spill and then pumped to the spill. At present, there are no further efforts in this direction.

Chlorine--

Chlorine has been reported to be controllable with foam (Buschman, 1975). The data is very limited however and the degree of vapor control is not well defined.

Inorganic Water Reactive Chemicals

This heading treats materials which are normally liquids. Two chemicals in this class have seen tests with foam. A formal test program was conducted with spills of SO_3 (Pfann, 1976), while cursory tests were conducted with SiCl_4 .

Sulfur Trioxide--

Under MCA sponsorship the manufacturers of SO_3 , oleum and related compounds, conducted extensive testing to find acceptable means of handling spills of these materials. A few very effective techniques were found which could be implemented in fixed installations. These were not acceptable for field use, however. Although foam left much to be desired it was the only technique of those available which had any merit.

Foam application to spills of SO_3 , oleum, etc., results in rapid destruction of the foam due to the aggressive water reaction. The reactivity with foam is considerably less aggressive than with water. However, the lessening of reaction is desirable since dilution is a basic method of mitigating a spill of this type of material.

Reaction with water converts SO_3 to H_2SO_4 , a hazardous material of itself but not of the same order as SO_3 . Additionally, it is a liquid aerosol, rather than a vapor, and its downwind travel is restricted. Aggressive water reactions force evolution of SO_3 along with H_2SO_4 . Foam acts to limit the release of SO_3 .

Silicon Tetrachloride--

SiCl_4 reacts with water to form SiO_2 and HCl . As with SO_3 , the acid aerosol is less hazardous than the tetrachloride.

In an actual spill situation foam was tried and abandoned (Hampson, 1976). It caused what was considered excessive fuming. No data were obtained to determine any change in downwind characteristics between a free spill and foam treatment.

SECTION 5

SCOPE OF WORK

The program to evaluate and develop foams for mitigating air pollution from hazardous material spills was divided into three tasks. Task I was the delineation of available systems, Task II involved field testing of available systems and Task III was the examination of novel foam systems.

TASK I - DELINEATION OF AVAILABLE SYSTEMS

The emphasis in the first task was to define the capabilities and limitations of existing foam technology, and to arrange this information in a manual form for use by both first-on-the-scene emergency personnel and on-site coordinators. This information would also serve to point out gaps in the data and indicate areas of need for improved or novel foam systems.

State-of-the Art Survey

To initiate the program a state-of-the-art survey was made. In this, a complete listing was made of all of the foam agents, both low and high expansion, which are currently commercially available. They were characterized as to their intended use and their physical and chemical properties. Performance data was solicited as to foaming ability, drainage, collapse rate and other pertinent data.

Simultaneously with this, solicitations were made to collect all available data on the use of foam for spill control, both field and in-plant use. A general literature survey was conducted. Data were solicited from those companies involved in foam systems, both manufacturers and system designers. Government agencies, principally EPA and the Coast Guard, but including NIOSH, OSHA and the Bureau of Mines, were surveyed. In addition, state agencies and major city fire departments were solicited for any information they had available.

The survey covered the chemical industry, primarily through appropriate trade organizations, the Manufacturing Chemists Association, American Petroleum Institute, The Chlorine Institute, Society of Plastic Engineers, American Gas Association and others. Those research organizations which have been active in hazard chemical spill work were covered, although most of the data from this source was also available through the sponsoring agencies.

Results of the Survey--

Thirty inquiries were sent to foam and foaming equipment manufacturers. Seventeen replied, with some declining to participate in the program. Those companies which responded are listed below:

1. Akron Brass Company
2. Allison Control, Inc.
3. American LaFrance
4. Bowman Distribution
5. Elkhart Brass Mfg. Co. Inc.
6. Feecon Corporation
7. Fire Boss
8. Fire-Chem Mfg. Co. Inc.
9. Huntington Laboratories, Inc.
10. Walter Kidde and Co. Inc.
11. Laurentian Concentrates, Ltd.
12. Mine Safety Appliances Co.
13. National Foam Systems, Inc.
14. Rockwood Systems Corporation
15. Santa Rosa Mfg. Co.
16. The Mearl Corporation
17. 3M Company

Of these seventeen, Akron Brass Company and Bowman Distribution stated that their products had no capabilities in this area.

Literature Search

The literature search included sources such as Chemical Abstracts, Dissertation Abstracts, Fire Research Abstracts and Reviews, and Industrial and Engineering Chemistry. Most of the references obtained from these sources pertained to the use of foams against burning materials.

More information was found on the use of aqueous film forming foams for spill control than any other type of foam agent. The basic hypothesis for vapor transfer resistance by thin films was initiated by Hederstrand (1924). Various investigators have contributed to the research and development of this approach. Tuve et al (1964) provided the first discussion with reference to aqueous film-forming foam.

Meldrum (1972) prepared a practical evaluation of aqueous film-forming foams and their utilization. White (1976) expanded the data of evaporative control by surfactant films by incorporating the temperature factor. The environmental problems posed by fluorochemicals were reported by Kroop and Martin (1974), but there has not been much further public data in this area. Archer (1955) investigated the effects of discontinuities in the film or vapor release. All of these relate to nonflowing liquid surfaces.

A listing of pertinent documents reviewed is given in the Bibliography appended to this report.

Matrix Preparation

The data gathered was compiled and analyzed. A matrix was prepared which listed those classes of materials for which there was data on vapor control by foam applications. The matrix assesses each type of foam for each material and establishes a priority for the foam systems with each applicable material.

As was expected, the data exhibited numerous gaps and in many cases was not incontrovertible. Theoretically, we might consider extrapolating the existing data but this could lead to marginal or even unacceptable recommendations. It appeared better to develop data through experimental work and then update the matrix.

The preliminary matrix is shown in Table 1.

Laboratory Program

Materials Selection--

The needs of the matrix after its initial development were clear. Definitive data was needed for those basic categories of chemicals which pose a vapor hazard to the environment or the on-the-scene personnel.

It was decided that the valid determination of the capability of foam can only be made with real materials. Thus, selected hazardous materials (representative of each class) were used for testing. These can only be safely handled in the laboratory. Thus the development of the basic data was done on a laboratory scale. Subsequent field testing was used to verify these data using simulant materials which could be released to the atmosphere.

Test materials were taken from liquefied gases, materials which have aggressive water reaction and volatile organics. Some materials can fall in two categories.

The initial liquefied gas selection came from the nonwater-reactive materials. The important properties were the boiling point and the vapor density. To span the range of both, three materials were selected. These were liquefied petroleum gas (B.P. -42°C , vapor specific gravity at 0°C - 1.5), ethylene (B.P. -104°C , vapor specific gravity at 0°C - 1.0) and 1,3 butadiene (B.P. -4°C , vapor specific gravity at 0°C - 1.9). By adding existing data for LNG (B.P. -161°C , vapor specific gravity at 0°C - 0.55) to these three, a range of boiling points from -161 to -4°C is provided, covering a specific gravity range from 0.55 to 1.9.

Three additional cryogenic materials were selected, ethylene oxide, chlorine, and ammonia. Ethylene oxide (B.P. 11°C , vapor specific gravity - 1.5) provided a liquified gas with measurable water solubility but with a low heat of solution. Chlorine (B.P. -34°C , vapor specific gravity - 2.4) served to represent a material with an acid reaction. Ammonia (B.P. -33°C , vapor specific gravity - 0.6) represents materials with an alkaline reaction. It also has an aggressive water reaction.

TABLE 1. MATRIX OF FOAM CAPABILITIES TO SUPPRESS OR OTHERWISE MINIMIZE THE RELEASE OF TOXIC OR FLAMMABLE VAPORS FROM SPILLED HAZARDOUS CHEMICALS AS LISTED

	Recommend.	Surfactant		Fluoro-		Alcohol	AFFF	Mech.
		Low Ex.	High Ex.	Protein	Protein			
i-octane	R	B+	A+	B+	B+	E-	C+	U
n-heptane	R	B+	A+	B+	B+	E-	C+	U
Cyclohexane	R	B+	A+	B+	B+	E-	C+	U
Hexane	R	B+	A+	B+	B+	E-	C+	U
Benzene	R	B+	A+	-	-	E-	ND	ND
Toluene	R	B+	A+	-	-	E-	ND	ND
Gasoline	R	B+	A+	B+	B+	E-	C+	U
Kerosene	R	B+	A+	B+	B+	E-	C+	C+
Naphtha	R	B+	A+	B+	B+	E-	C+	U
Methanol	R	E-	E-	E-	E-	A+	E-	-
i-propanol	R	E-	E-	E-	E-	A+	E-	-
Butanol	R	E-	E-	E-	E-	A+	E-	-
Butyl Cellosolve	ND	ND	ND	U	ND	ND	ND	U
Acetone	R	E-	E-	E-	E-	A+	E-	ND
Methyl Ethyl Ketone	ND	U	U	U	ND	ND	ND	ND
Methyl i-butyl Ketone	R	B+	A+	U	ND	ND	ND	ND
Lacquer Thinner	ND	U	ND	ND	ND	ND	U	ND
Paint Thinner	ND	U	ND	ND	ND	ND	U	ND
SiCl ₄	R	C+	C+	C+	C+	ND	F-	ND
i-amyl Alcohol	ND	U	U	U	ND	ND	ND	ND
Ethyl Acetate	ND	U	-	-	U	ND	ND	ND
Butyl Acetate	ND	U	-	-	U	ND	ND	ND
i-propyl Acetane	ND	U	-	-	U	ND	ND	ND
Methyl Acrylate	R	B+	A+	ND	U	ND	ND	ND
Methyl Methacrylate	R	B+	A+	ND	U	ND	ND	ND
SO ₃	R	C+	C+	C+	C+	ND	F-	ND
Acetic Acid	R	A+	B+	ND	ND	ND	ND	U
Caproic Acid	ND	U	ND	ND	ND	ND	ND	U
Methyl Bromide	ND	U	U	ND	ND	ND	ND	ND
Butyl Bromide	R	A+	U	ND	ND	ND	ND	ND
N,N'-dimethyl Formamide	ND	U	E-	ND	ND	ND	ND	ND
Tetrachloroethane	R	B+	A+	ND	ND	ND	ND	ND
n-Octanol	R	B+	A+	B+	+	-	ND	U
Tetrahydronaphthalene	R	B+	A+	E-	ND	ND	U	ND
LNG	R	E-	A+	F-	F-	F-	F-	ND
Chlorine	R	B+	A+	B-	B-	ND	E-	ND
Ammonia	R	A+	A+	B+	B+	ND	E-	ND

IDENTIFICATION OF SYMBOLS

- + Data available indicating vapor pollution control
- Data available indicating no vapor pollution control
- U Limited data available-capabilities uncertain
- ND No Data

- R Foam use recommended over spill
- ND Insufficient Data

- A Best foam formulation
- B Next best foam formulation
- C Acceptable in some situations; see text
- E Unsuitable foam formulation
- F Deleterious foam formulation

Foams are best when ambient is above freezing, winds are less than 15 knots and there is no precipitation. Foam can be employed as long as it can be generated. Temperature effects will be seen first in generator operation. Rain will exaggerate collapse but will not impair foam generation or flow. Wind above 10 mph will lift foam. Downwind barriers will assist in holding foam in place. Low expansion is more tolerant of weather than high expansion but where high expansion is shown to be the best choice the inability to build thickness should be the only factor considered in switching.

To include aggressive water reactants which are acidic, two materials -- sulfur trioxide and anhydrous hydrogen fluoride -- were selected. A listing of the properties for the liquefied gases or water reactive chemicals used in the program is given in Table 2.

Although the liquefied gases and water reactive liquids offer interesting materials from the standpoint of foam application, the large number of volatile chemicals do not exhibit either property. These materials are mainly volatile organics. In the work prior to this study, three properties have been shown to be important -- molecular weight, water solubility and vapor pressure. There were indications also that the degree of saturation might be a significant variable, along with the chemical arrangement straight chain or cyclic.

The selecting of compounds to cover the volatile organics was restricted to those materials whose vapor pressure at 20°C is greater than 0.5cm. Polar compounds were given token representation since it had already been established that only alcohol type foams were applicable.

Due to the large number of chemicals falling in this category, the selection was made to cover the three variables deemed most significant by the dielectric constant, vapor pressure and water solubility. Final selection was made after the initial matrix was developed.

For the polar group the dielectric constant was the prime variable, followed by vapor pressure and water solubility. The range of variables was covered with four materials. Three materials were selected to cover a range of dielectric constants from about 2.5 to 5.01. Available data indicated that below 2, materials would behave the same as nonpolar compounds. Above a dielectric constant of 4, non alcohol types of foam are seriously degraded. One compound of high dielectric constant and high water solubility was selected to complete this category. The selected polar materials are listed in Table 3. They cover a range of molecular weights from 58 to 116, vapor pressure varies from 1 cm to 55 cm, and water solubility from 0.5 g/cc to complete miscibility.

With nonpolar compounds, the dielectric constant is less significant since most are below a value of 3. Vapor pressure and water solubility were felt to be the principle variables.

Table 4 identifies the selected nonpolar candidates. The first three on the list are of the same family, differing in vapor pressure and molecular weight. Cyclohexane has properties similar to benzene except for its water solubility and the fact that it is a five membered ring.

N-Octane was selected as a representative of long chain aliphatic material of low water solubility.

Selection of Foam Chemicals--

The selection of the foams used in the laboratory tests came from those in wide use by the five service. To insure objective selection, foam characterization was performed by University Engineers on independent laboratory.

TABLE 2. PROPERTIES OF LIQUEFIED GASES OR WATER REACTIVE CHEMICALS

<u>Property</u>	<u>Ethylene</u>	<u>Propane</u>	<u>1,3 Butadiene</u>	<u>Ethylene Oxide</u>	<u>Ammonia</u>	<u>Chlorine</u>	<u>Hydrogen Fluoride</u>	<u>Sulfur Trioxide</u>
Boiling Point (°C)	-103.7	-42.1	-4.4	10.6	-33.4	-34.1	19.5	44.8
Latent Heat of Vaporization (cal/g)	115.4	101.8	100	138.5	327	68.7	80.5	118.5
Specific Heat (cal/g H ₂ O)	68	40	23	10	36	36	--	--
Vapor S.G. (air - 1.0)	1	1.5	1.9	1.5	.6	2.4	.7	2.86
Liquid S. G. (water - 1.0)	.569	.590	.621	.869	.682	1.424	.992	1.9224
Heat of Solution (cal/g)	--	--	--	-34	-129	--	-734.6	-504
Molecular Weight	28	44	54.09	44.5	17.03	70.91	20.01	80.06

TABLE 3. CANDIDATE POLAR MATERIALS

<u>Name</u>	<u>Dielectric Constant</u>	<u>Vapor Pressure (mm)</u>	<u>Water Solubility (g/cc)</u>	<u>Molecular Weight</u>
Acetone	20.7	180	Miscible	58
n-butyl acetate	5.01	10	0.5	116
Ethyl ether	4.41	550	7.5	74
Triethylamine	2.42	77	1.5	101

TABLE 4. CANDIDATE NONPOLAR MATERIALS

<u>Name</u>	<u>Dielectric Constant</u>	<u>Vapor Pressure (mm)</u>	<u>Water Solubility (g/cc)</u>	<u>Molecular Weight</u>
Cyclohexane	2.05	100	0.0001	84
Benzene	2.28	95	0.080	78
Toluene	2.38	35	0.047	92
Ethyl benzene	2.41	10	0.014	106
n-octane	1.95	14	0.0015	114

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It was their task to obtain samples of all major commercially available foam agents of each class -- protein, fluoroprotein, AFFF, alcohol and surfactants, and for each applicable expansion ratio, establish the important properties of drainage, collapse, pH and surface tension. For each property, standard tests were used if available. For low expansion foams, tests are established and detailed in NFPA 11 and 11B, and appropriate federal and Underwriters Laboratories specifications. High expansion, however, did not have a standard test for drainage and collapse. This has been corrected since this program was conducted. For this program, the test in use at the time by MSAR was used. This test measures drainage and collapse of a column of 500:1 expansion foam 61 cm in diameter by 91 cm in height. Based upon these data, representative agents were selected for use in the laboratory test program.

Commercial fire fighting foams were ordered for testing by University Engineers from authorized distributors of each manufacturer. Foam agents were purchased of the following manufacturers:

1. Rockwood - protein, alcohol and surfactant
2. Mearl - protein, fluoroprotein and surfactant
3. National - protein, fluoroprotein, alcohol, AFFF and surfactant
4. Huntington - surfactant
5. Laurentain (Lorcon) - protein, fluoroprotein, alcohol, AFFF and surfactant
6. 3M - AFFF
7. Kidde - surfactant
8. Elkhart - surfactant
9. MSA - surfactant

Akron Brass, a manufacturer of surfactant foams, declined to participate and our inquiries to Jefferson Chemical (Firesorb) and Western Fire (Firechem) were not answered.

The results for low expansion foams except AFFF's are shown in Table 5. Data was obtained using a 6 gpm nozzle designed according to a joint Army, Navy and Air Force standard (JANAF). The drainage data was obtained using the test described in NFPA 11.

The results for AFFF's are given in Table 6. The same low expansion foam equipment and tests were used for the AFFF tests as were used for the other low expansion agents.

Table 7 presents the results for high expansion foams. It should be noted that in some cases the reported values for each category are not consistent with those reported by the manufacturers. The data has been derived using standard equipment and accepted techniques. It is presented here as reported to MSAR by the independent testing laboratory.

Two foam agents were chosen for the laboratory test program from each of the protein, fluoroprotein, alcohol and AFFF manufacturers. Due to effective regulation of the industry, most agents are somewhat comparable.

TABLE 5. PROPERTIES OF CANDIDATE FOAM AGENTS

Foam	Expansion Ratio in Lab	% Addition	Expansion Ratio in Field	% Addition	pH Standard Sol'n.	Surface Tension dynes/cm	Quarter Drainage (min)
Protein 3%							
Rockwood	4.1	3.0	5.9	3.4	7.5	50.0	0.66
Mearl	4.3	3.0	6.1	4.8	7.1	49.0	0.90
Lorcon	3.7	3.0	5.9	4.4	7.0	50.0	0.95
National	4.4	3.0	4.9	4.4	7.6	40.0	1.23
Protein 6%							
Rockwood	4.2	6.0	4.5	5.6	7.1	48.7	0.98
Mearl	3.9	6.0	7.1	5.2	7.3	46.9	0.92
Lorcon	4.6	6.0	5.1	5.2	7.4	47.5	0.45
National	4.3	6.0	6.5	5.4	7.5	46.4	1.41
Fluoroprotein 3%							
Lorcon	3.3	3.0	4.6	3.8	7.1	29.4	0.37
National	3.3	3.0	4.2	3.8	7.6	30.2	0.54
Fluoroprotein 6%							
Mearl	4.2	6.0	3.7	5.2	7.3	27.6	0.37
National	4.7	6.0	5.7	5.4	7.7	27.7	0.63
Alcohol							
Rockwood	2.7	6.0	5.9	6.0	9.4	51.1	1.25
Lorcon	could not educt -- viscosity too high			5.4	5.5	38.2	0.42
National	3.1	6.0	3.8				
Surfactant							
Elkhart	-	-	6.8	5.8	5.9	32.1	0.45
Huntington	-	-	8.6	5.4	8.4	37.0	0.69
Lorcon	-	-	4.0	6.0	8.2	26.5	0.53
Rockwood	-	-	4.0	6.4	7.3	25.6	0.70
Mearl	-	-	4.5	7.1	5.9	25.3	1.25
National	-	-	3.5	6.4	8.6	26.2	1.29
Kidde	-	-	4.0	6.7	6.7	26.2	1.68
MSA	-	-	4.0	6.5	6.8	25.6	1.69

TABLE 6. EXPANSION AND DRAINAGE OF AFFF FOAM SYSTEMS

<u>Foam Agent</u>	<u>Addition Rate (%)</u>		<u>Expansion</u>		<u>Quarter Drainage (min)</u>	<u>pH</u>	<u>Surface Tension (dynes/cm)</u>
	<u>Laboratory</u>	<u>Field Test</u>	<u>Laboratory</u>	<u>Field Test</u>			
National Aero Water Plus 3	3.0	4.4	5.9	9.9	1.42	7.9	20.3
Lorcon Foam L	3.0	4.2	4.6	7.2	0.73	7.2	19.4
3M Light Water 3%	3.0	4.6	6.6	11.1	2.17	8.2	18.7
National Foam AFFF 6%	6.0	7.0	5.1	7.6	0.90	9.6	19.2
3M Light Water 6%	6.0	6.6	5.5	7.4	0.76	7.9	18.6

TABLE 7. PROPERTIES OF HIGH EXPANSION FOAM SYSTEMS

Foam Agent	Addition Rate (%)	pH 10% Soln.	Surface Tension Dynes/cm	Drainage % in Minutes			Quarter Drainage Time (min)	Collapse Rate (In/hr)
				10	20	30		
Flame Out (Huntington)	2	8.4	37.0	97	100	100	1	150
Emulsiflame (Elkhart)	2	5.9	32.1	95	100	100	1	75
Jet X (Rockwood)	2	7.3	25.6	85	94	97	2	70
Ultra X (Mearl)	2	5.9	25.3	49	76	86	5	60
Full X (Lorcon)	2	8.2	26.5	45	67	75	6	8
Ultra Foam (MSA)	2	6.8	25.6	20	40	55	13	8
Hi Ex (National)	2	8.6	26.2	21	44	58	12	8
Hi X (Kidde)	2	6.7	26.2	18	38	53	14	8

TABLE 8. REPRESENTATIVE LOW EXPANSION FOAMS

<u>Foam Type</u>	<u>Foam Agent</u>	<u>Surface Tension (dynes/cm)</u>	<u>Quarter Drainage Time (min)</u>
Protein 3%	Rockwood	50	.66
Protein 3%	National	40	1.23
Protein 6%	Lorcon	47.5	.45
Protein 6%	National	46.4	1.41
Fluoroprotein 3%	Lorcon	29.4	.37
Fluoroprotein 3%	National	30.2	.54
Fluoroprotein 6%	Mearl	27.6	.37
Fluoroprotein 6%	National	27.7	.63
Alcohol	National	38.2	.42
Alcohol	Rockwood	51.1	1.25
Surfactant	Lorcon	26.5	.53
Surfactant	Huntington	37.0	.69
Surfactant	Mearl	25.3	1.25
Surfactant	MSA	25.6	1.69
AFFF 3%	National	20.3	1.42
AFFF 6%	3M	18.6	0.76

The hydrocarbon surfactants are essentially unregulated and a broad spectrum of materials are available. The existing data indicates that only slow draining materials should be selected. It appeared important, however, to fully define capability as a function of drainage and collapse for the information of potential users. Four surfactant foam agents were chosen for laboratory testing to encompass the available foam properties.

All the foam agents chosen are listed in Table 8. In each case, they reflect the range of drainage and surface tensions in each category.

Test Program--

With the selection of the test chemical and the foams to be evaluated, the laboratory test program was initiated. Three separate test sequences were used, one for low expansion foam, one for medium expansion foam and one for high expansion foam. For low expansion materials, expansions of 2.5:1 were evaluated. The low expansion foams were produced using a laboratory blender. Medium expansion foams of 250:1 were produced with an air aspirating generator. High expansion foams at 500:1 were produced with an induced air generator.

Laboratory Test Procedures for Volatile Organics--The test sequence for this class of materials paralleled one successfully employed in previous work. A 250 ml volume of the chemical to be evaluated was placed in a 30 cm diameter glass vessel. A foam layer was applied to the surface. The thickness was 5 cm for low expansion foams, 30 cm for medium expansion and 50 cm for high expansion. The vapor concentration above the foam was continuously monitored and recorded.

Sensors were placed in the laboratory test vessel to measure vapor permeation through the foam. The sensors consisted of the MSA Series 500 Combustible Gas Detection System and chart recorders to continuously monitor vapor concentration versus time above the foam layer. Additional gas detectors were provided to measure the vapor concentration versus time within the foam. This is an equilibrated test sequence that defined the rate of permeation through the foam and the time period for which a given thickness of foam provided protection.

By using a specific thickness with no make up, the influence of drainage and collapse rate on the length of protection was defined. Relating the rate of permeation for a wide variety of materials to their properties, such as water solubility and vapor pressure, permits the interpolation of the data to at least all of the materials in each subgroup if not the complete class.

Laboratory test procedures for liquefied gases--The test sequences for these materials were similar to those for the volatile materials. Vaporization rate and dispersion are the important factors. Since foam can neither develop pressure over the spill or completely exclude radiant energy, spills of these materials boil even with a foam cover. The lack of water solubility means a continuous rapid release of gas. Foam isolates the surface, reduces the temperature differential and warms the gases.

The laboratory test sequence for insoluble liquefied gases was similar to that used for volatile organics. A glass vessel 30 cm in diameter with a volume of 33 liters was used. The glass vessel was insulated and the chemical to be tested was added until a 1.3 cm liquid layer existed in the bottom of the vessel. Foam was added to the depths specified previously. Because of problems of weighing or measuring the volume of off gasing from the liquefied gas, only visual observations could be made. Notes were taken on the intensity of boiling at the foam-liquid interface as well as the behavior of the foam layer. For reactive liquids the extent of foam degradation was qualitatively noted.

During the test program, conditions which could be encountered in the field, wind, rain, temperature, etc., were not factored in. The laboratory tests were based upon reproducible conditions to obtain results which can be evaluated, analyzed and compared.

Laboratory test results for volatile organics--The test method used involved an uncovered test chamber and continuous monitoring of the vapor concentration just above the collapsing foam column. This test method simulated the real conditions of unrestricted vertical dissipation and the dynamic behavior involved during foam collapse. In previous studies the test procedure for evaluating the vapor mitigation properties of foams involved a closed test chamber in which samples were taken at a constant height above the spill surface independent of the collapsing foam level. This method gave abnormal readings since vapor dissipation was restricted in the vertical direction. The vapor concentration just above the foam layer was not obtained. One real condition which is simulated by the uncovered test chamber is that of swirling; small eddys found at the liquid-air interface. Swirling effects can change the vapor concentration above a spill by several hundred percent; an important consideration especially near the lower explosive limit (LEL).

One data point of importance was the height above a spill corresponding to the LEL. Figure 1 is a graph of the benzene vapor concentration versus height above a benzene spill surface with no foam cover. The test is done in a 30 cm diameter by 45 cm high glass battery jar. As the detector head is lowered into the test chamber the LEL for benzene is found to occur between 9 to 18 cm above the spill surface. The vapor concentration falls off very quickly above 18 cm. A covered test chamber increased the height where the LEL is reached to approximately 30 cm. The graph indicates that even when considering swirling effects, the benzene has a maximum height at which the LEL can occur.

By following the collapsing foam column, the vapor concentration leaving the foam surface can be recorded. It can be considered that when the residual foam thickness is below the critical LEL height, the foam has lost its effectiveness.

Figure 2 shows a graph of the benzene vapor concentration for a medium expansion foam column at 10 cm and 20 cm above the spill, as well as the vapor concentration above the collapsing foam column. The initial foam thickness was 30 cm. At 10 cm all the foams (Emulsiflame, Lorcon, MSA) had

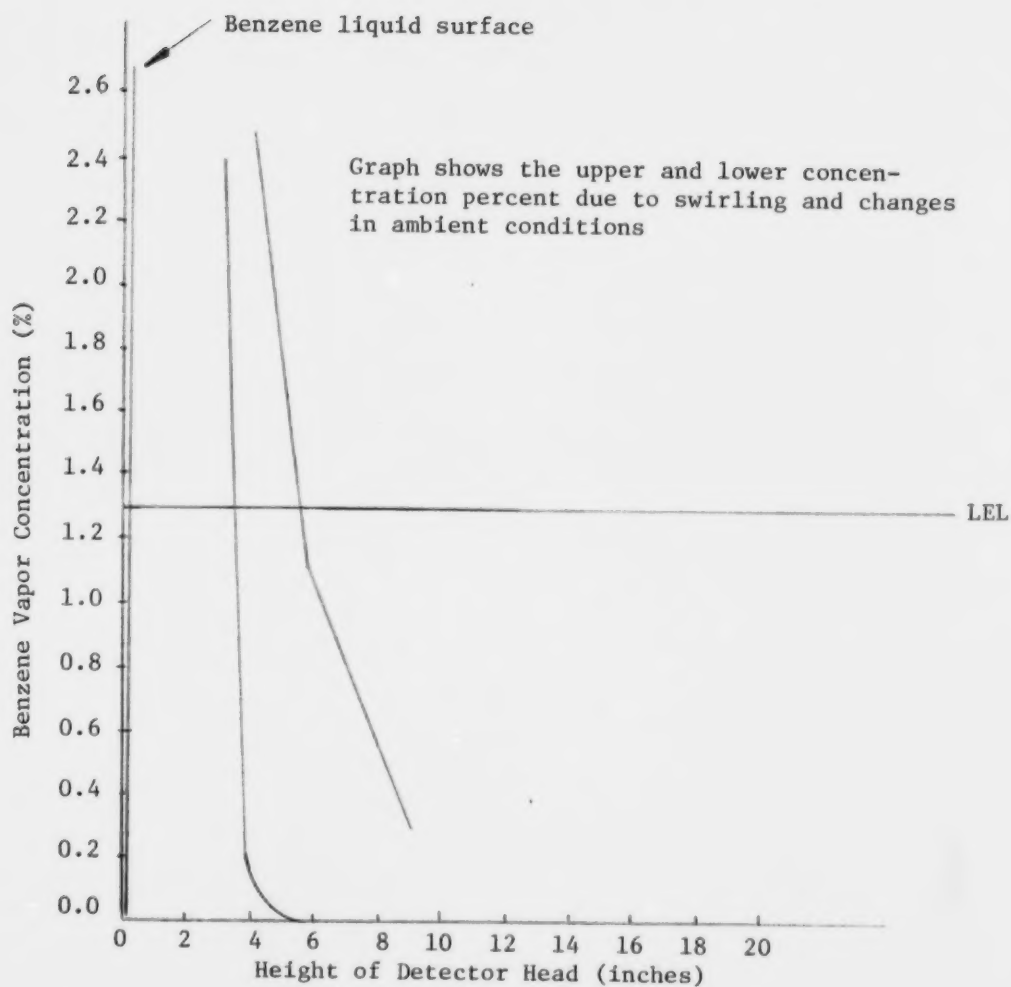


Figure 1. Benzene vapor concentration vs detector height

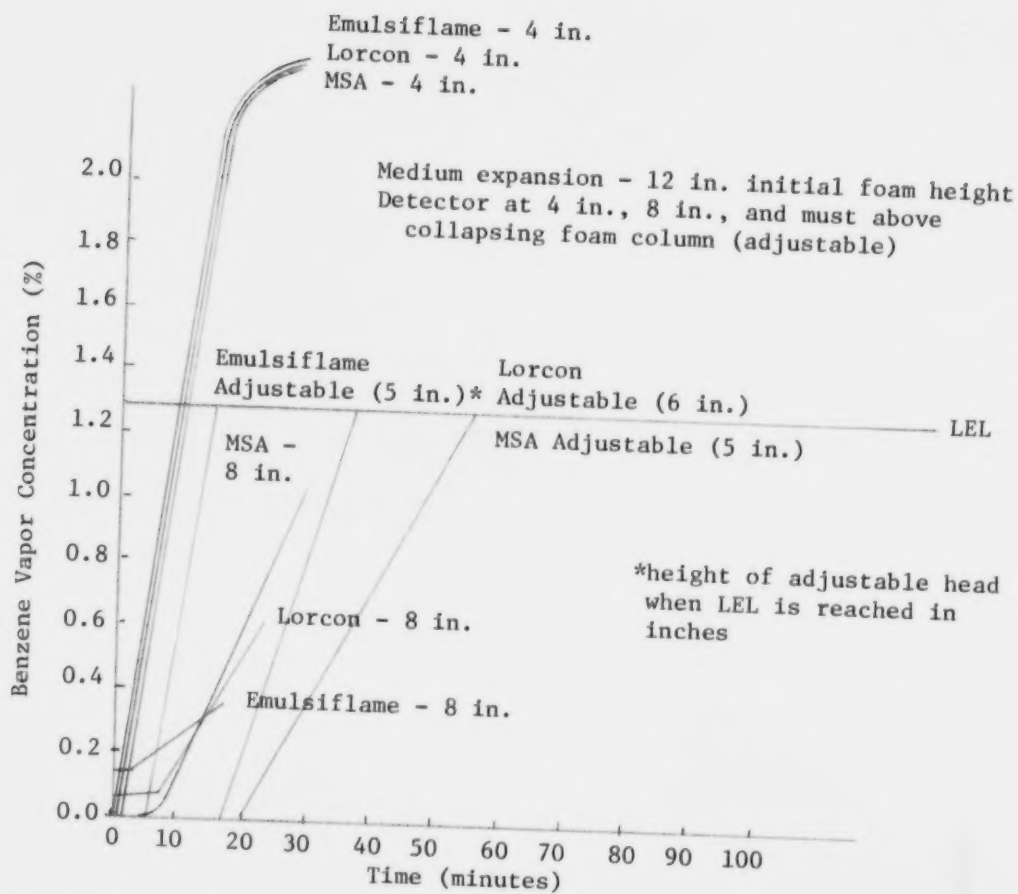


Figure 2. Benzene vapor concentration percent vs time for MSA, Lorcon, Emulsiflame

the same rate of increase in the benzene vapor concentration. At 20 cm the height at which the LEL is reached above the collapsing foam column is approximately the same.

The mitigation properties of medium expansion foams can be related to the collapse rate, rather than the drainage rate. It should be noted, however, that a foam with a dry cellular structure (fast drainage, slow collapse) is less resistant to environmental effects and these influences could materially alter the capability of the foam.

The aqueous film-forming foams (AFFF) results are shown in Figure 3. A 5 cm cover of low expansion and 30 cm of medium expansion foam has about the same vapor mitigation time. The 3% National Foam which had improved vapor mitigation time due to its slower collapse rate. When comparing the mitigation time of the low expansion with a 5 cm foam cover to that of medium expansion at 10 cm above the spill, the low expansion controlled the vapor permeation through the foam better than medium expansion. The low expansion foam layer can become saturated, wherein the LEL will be above the 5 cm foam thickness. In the medium expansion foam, as long as the foam height remained above the critical LEL height of 9 to 18 cm, the LEL concentration will occur within the foam mass.

Figure 4 is a graph of the vapor concentration of the cyclic hydrocarbons (cyclohexane, benzene, toluene, and ethyl benzene) versus time for the high expansion surfactant foams (MSA Ultra, Lorcon Full-Ex, Emulsiflame). Octane behaved like ethyl benzene in terms of its vapor mitigation time. The graph shows the mitigation time provided by a 50 cm foam blanket. The polar hydrocarbons (acetone, n-butyl acetate, ethyl ether, and triethylamine) caused all the high expansion foams to collapse, rapidly. From Figure 4 the slow draining, slow collapsing MSA Ultrafoam had the best mitigation time, the fast draining, slow collapsing Lorcon Full-Ex foam had an intermediate mitigation time and the fast draining, fast collapsing Emulsiflame had the shortest mitigation time.

The medium expansion data for the surfactant and Aqueous Film Forming Foams (National 3% and Light Water 6%) are given in Figures 5 and 6. Once again, only the nonpolar hydrocarbons are shown since the polar hydrocarbons caused rapid foam collapse. In general, the mitigation times follow the collapse and drainage rate.

The data for low expansion foams is shown in Figures 7-10. The expansion rate was approximately 2.5:1 and the initial foam height was 5 cm. The foam categories are: 3% regular protein, 6% regular protein, 3% fluoroprotein, 6% fluoroprotein, 6% alcohol, 6% surfactant, 3% AFFF and 6% AFFF. In Figure 7 the mitigation times of the various foams above a simulated acetone spill are shown. The Rockwood 6% alcohol foams has a very long mitigation time. The National Aerofoam 99-6% (alcohol), 3% National regular protein and 6% National regular protein have intermediate mitigation times while the remaining foam agents show short mitigation times. In Figure 8 the various foams are shown with benzene. In this case the 6% surfactant, 3% AFFF and 6% AFFF show the shortest mitigation times, while the 3% National fluoroprotein and 6% Lorcon regular protein show intermediate times and the remaining

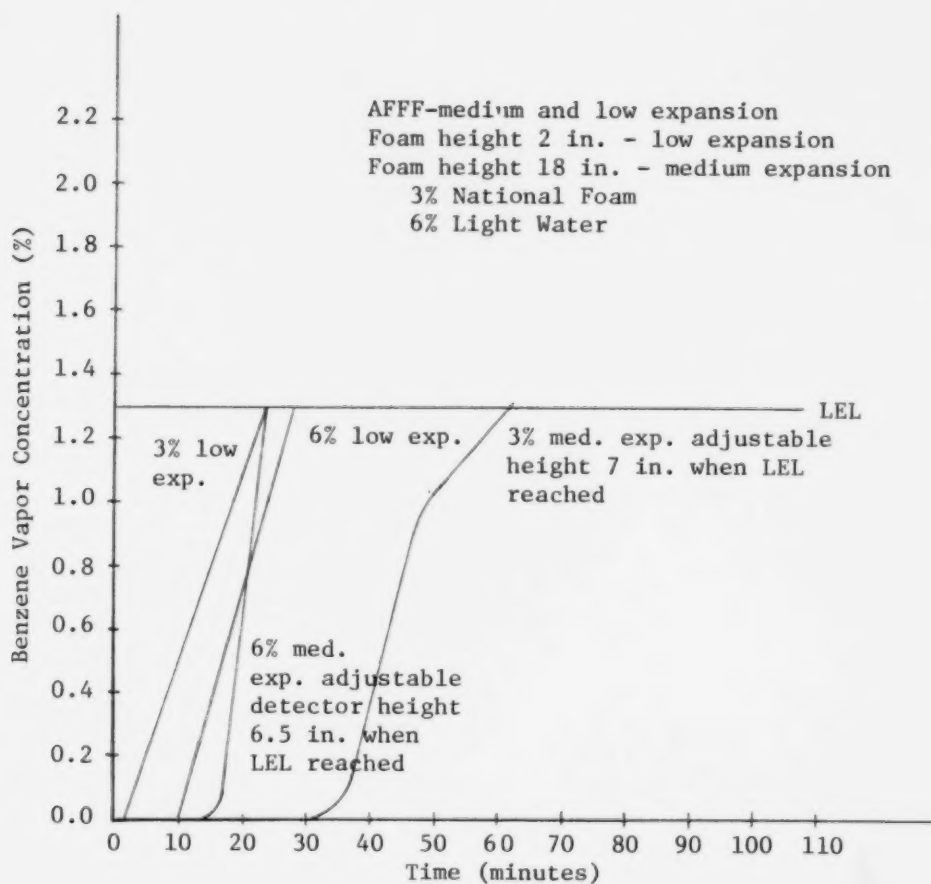


Figure 3. Benzene vapor concentration vs time

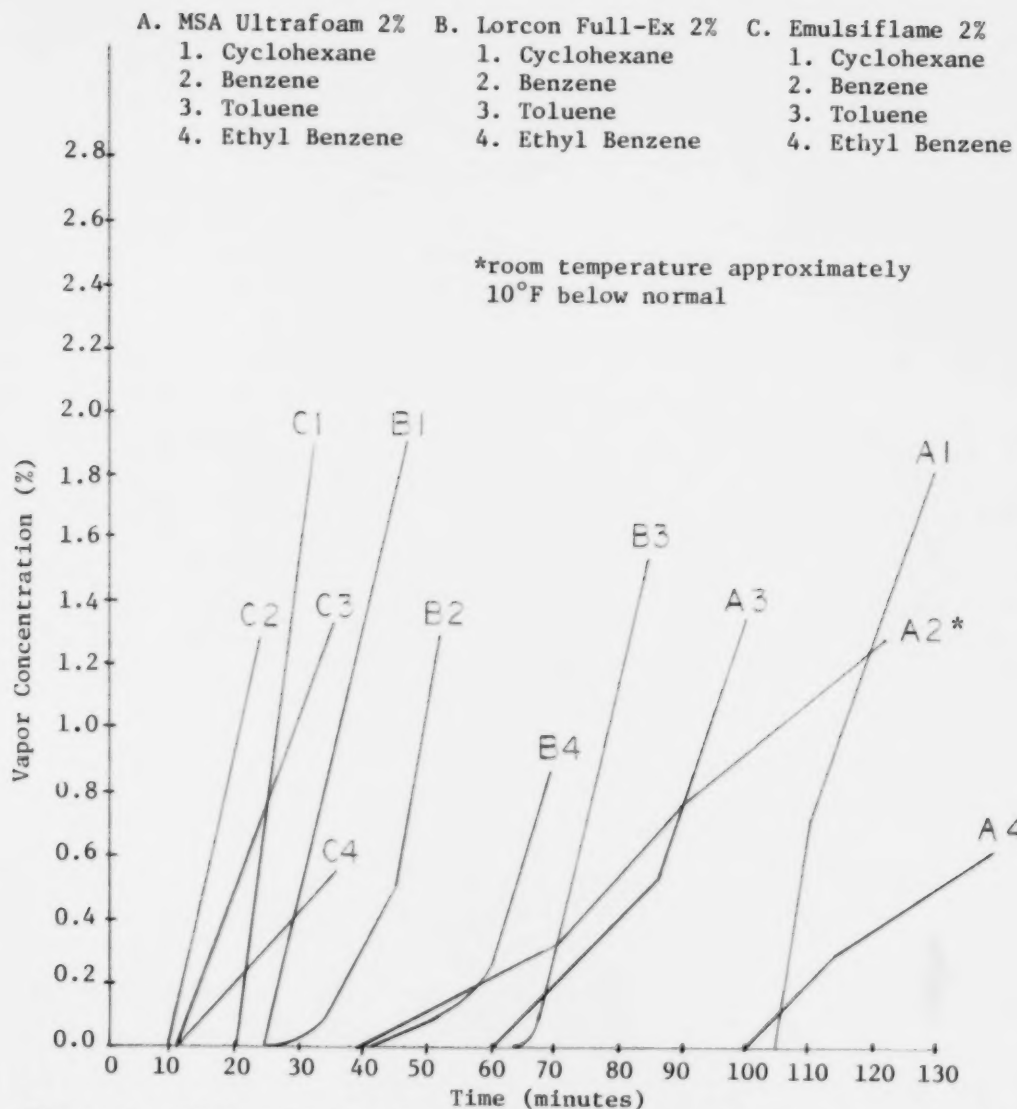


Figure 4. High expansion foams with nonpolar hydrocarbons
(initial foam height was 20 in.)

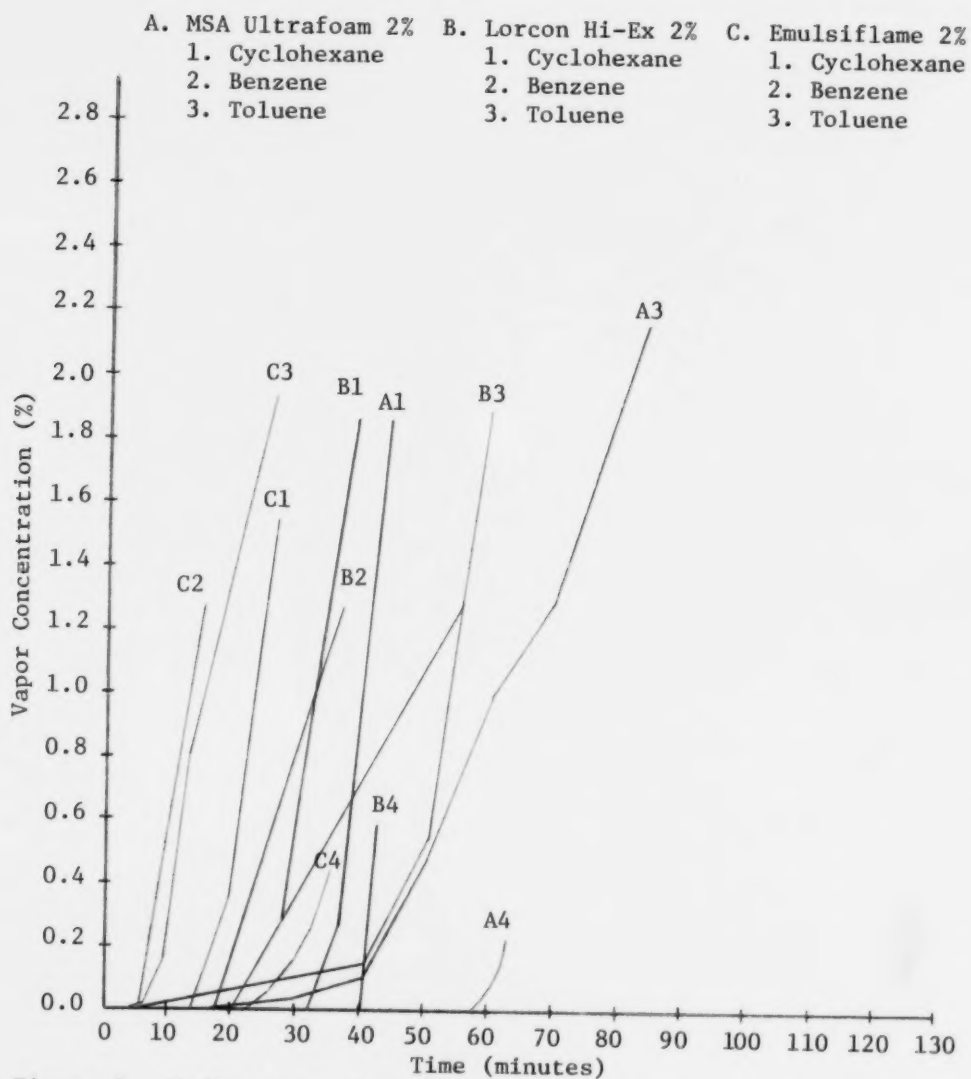


Figure 5. Medium expansion foams with nonpolar hydrocarbons
(initial foam height was 12 in.)

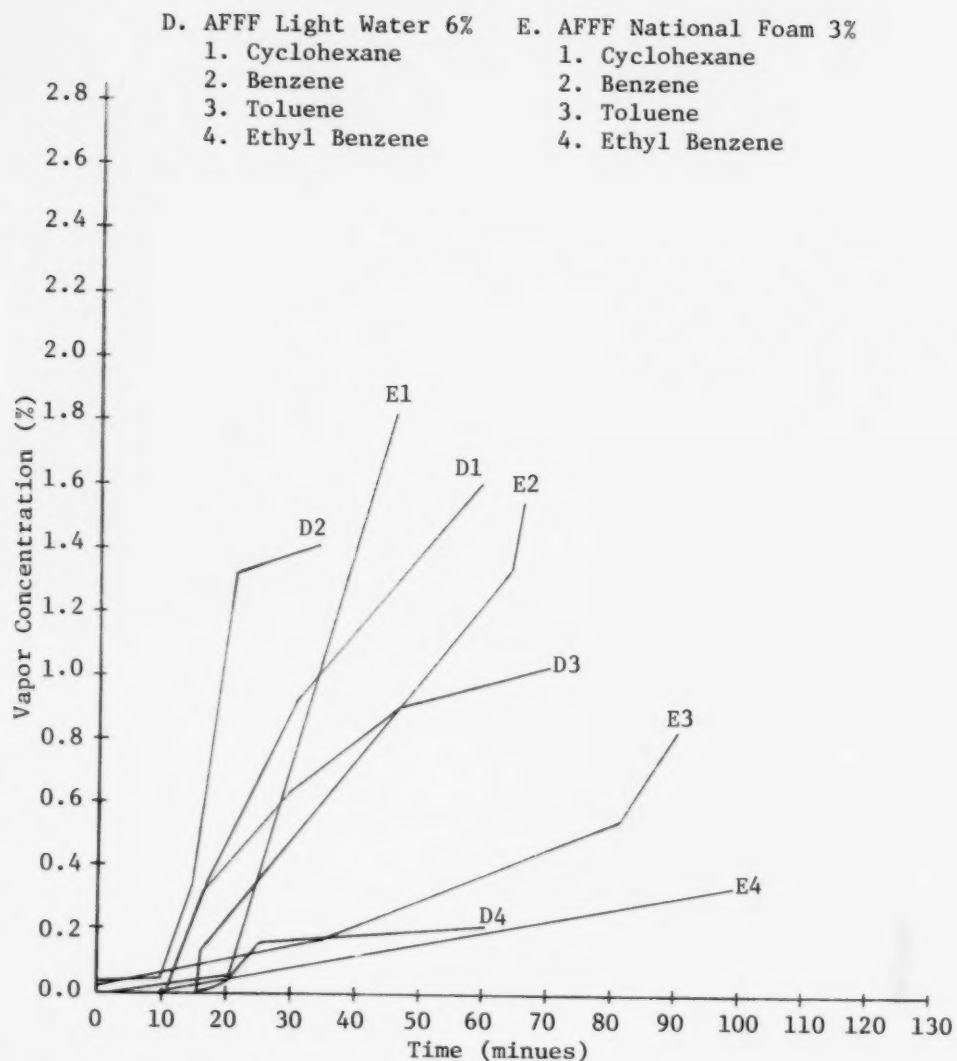


Figure 6. Medium expansion foams with nonpolar hydrocarbons
(initial foam height was 12 in.)

- | | |
|------------------------|-----------------------------|
| 1. National 3% Regular | 9. Rockwood Alcohol 6% |
| 2. Rockwood 3% Regular | 10. National Aerofoam 99-6% |
| 3. National 6% Regular | 11. Flame-Out 6% |
| 4. Lorcon 6% Regular | 12. MSA Ultrafoam 6% |
| 5. Lorcon 3% FP | 13. Rockwood Jet-X 6% |
| 6. National XL-3% FP | 14. Lorcon Full Ex 6% |
| 7. Mearl 6% FP | 15. National 3% AFFF |
| 8. National XL-6% FP | 16. 3M Light Water 6% AFFF |

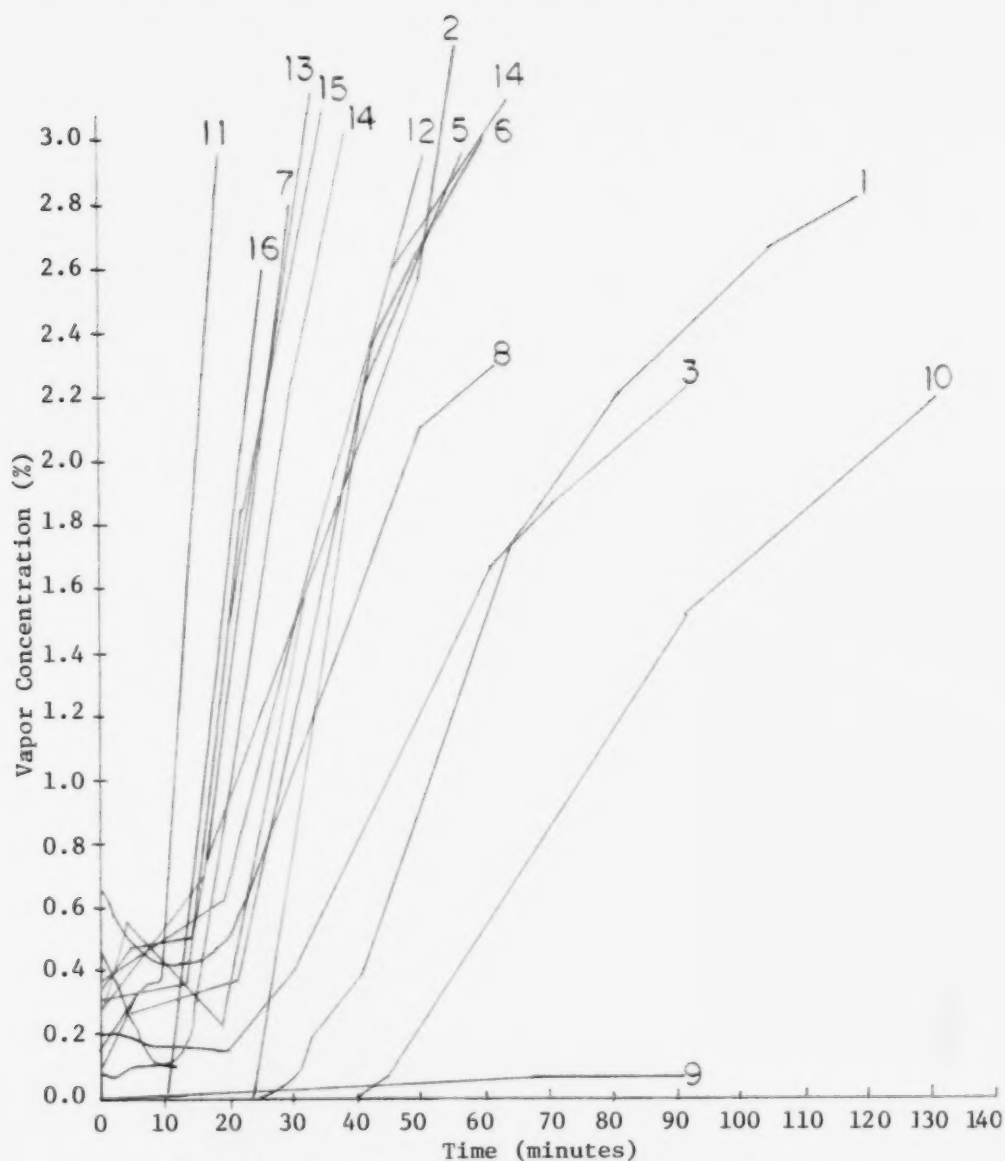


Figure 7. Acetone with low expansion foam
(initial foam height was 2 in.)

- | | |
|------------------------|-----------------------------|
| 1. National 3% Regular | 9. Rockwood Alcohol 6% |
| 2. Rockwood 3% Regular | 10. National Aerofoam 99-6% |
| 3. National 6% Regular | 11. Flame-Out 6% |
| 4. Lorcon 6% Regular | 12. MSA Ultrafoam 6% |
| 5. Lorcon 3% FP | 13. Rockwood Jet-X 6% |
| 6. National XL-3% FP | 14. Lorcon Full Ex 6% |
| 7. Mearl 6% FP | 15. National 3% AFFF |
| 8. National XL-6% FP | 16. 3M Light Water 6% AFFF |

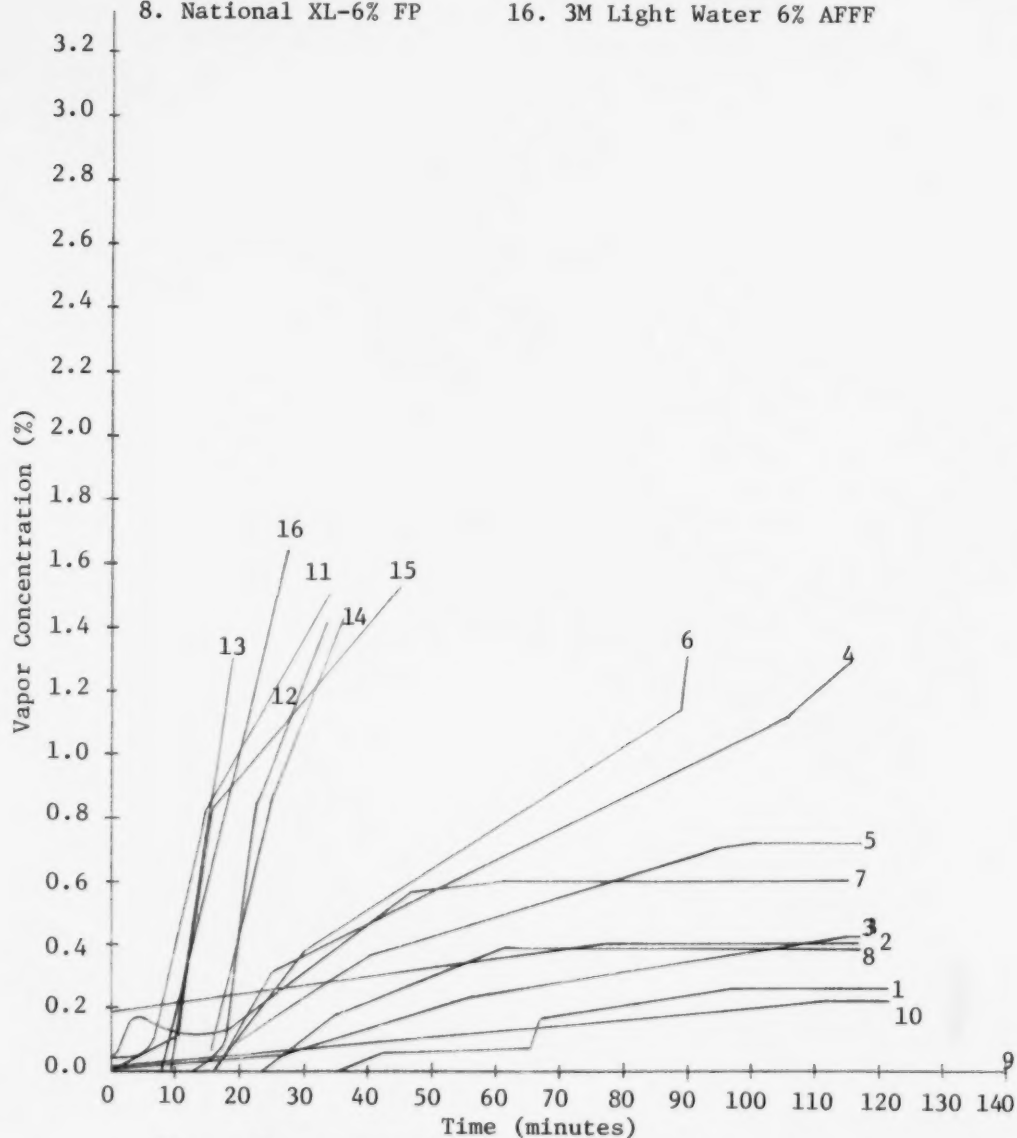


Figure 8. Benzene with low expansion foam
(initial foam height was 2 in.)

- | | |
|------------------------|-----------------------------|
| 1. National 3% Regular | 9. Rockwood Alcohol 6% |
| 2. Rockwood 3% Regular | 10. National Aerofoam 99-6% |
| 3. National 6% Regular | 11. Flame-Out 6% |
| 4. Lorcon 6% Regular | 12. MSA Ultrafoam 6% |
| 5. Lorcon 3% FP | 13. Rockwood Jet-X 6% |
| 6. National XL-3% FP | 14. Lorcon Full Ex 6% |
| 7. Mearl 6% FP | 15. National 3% AFFF |
| 8. National XL-6% FP | 16. 3M Light Water 6% AFFF |

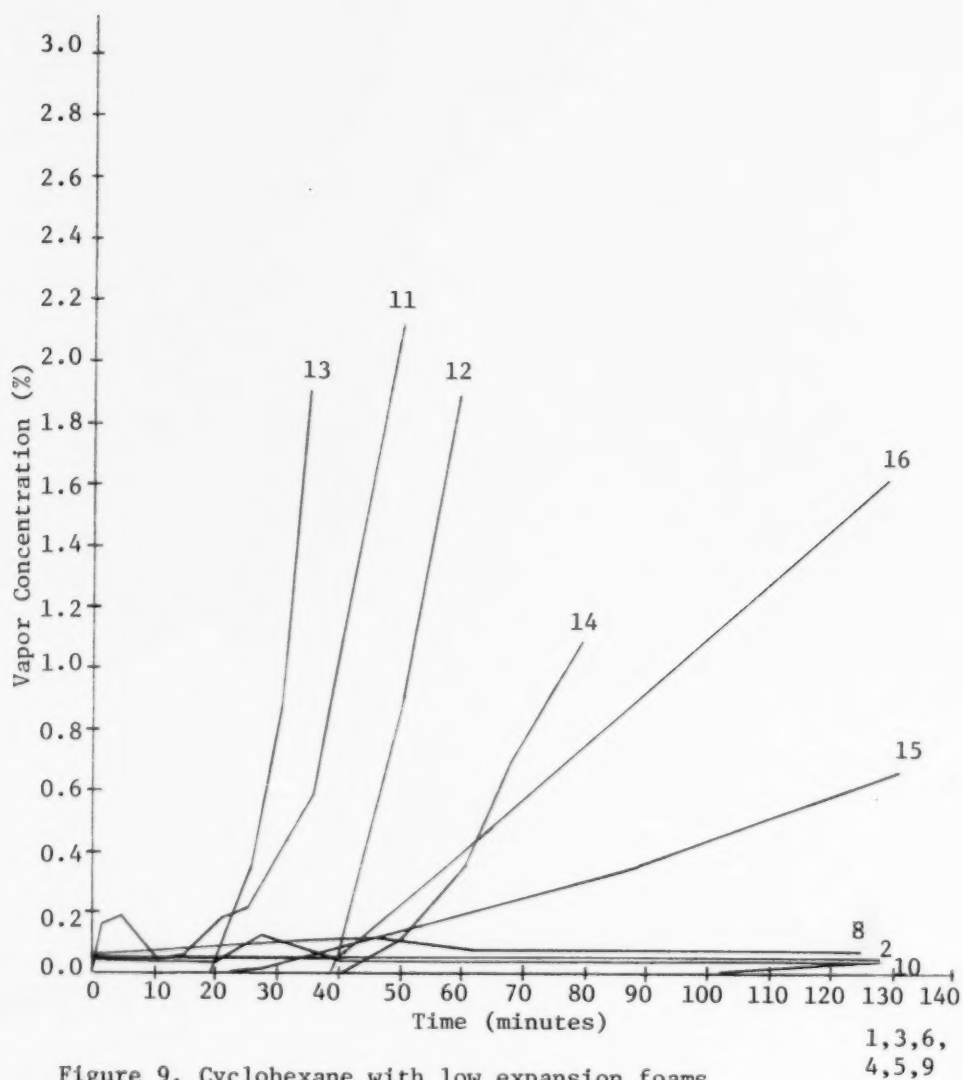


Figure 9. Cyclohexane with low expansion foams
(initial foam height was 2 in.)

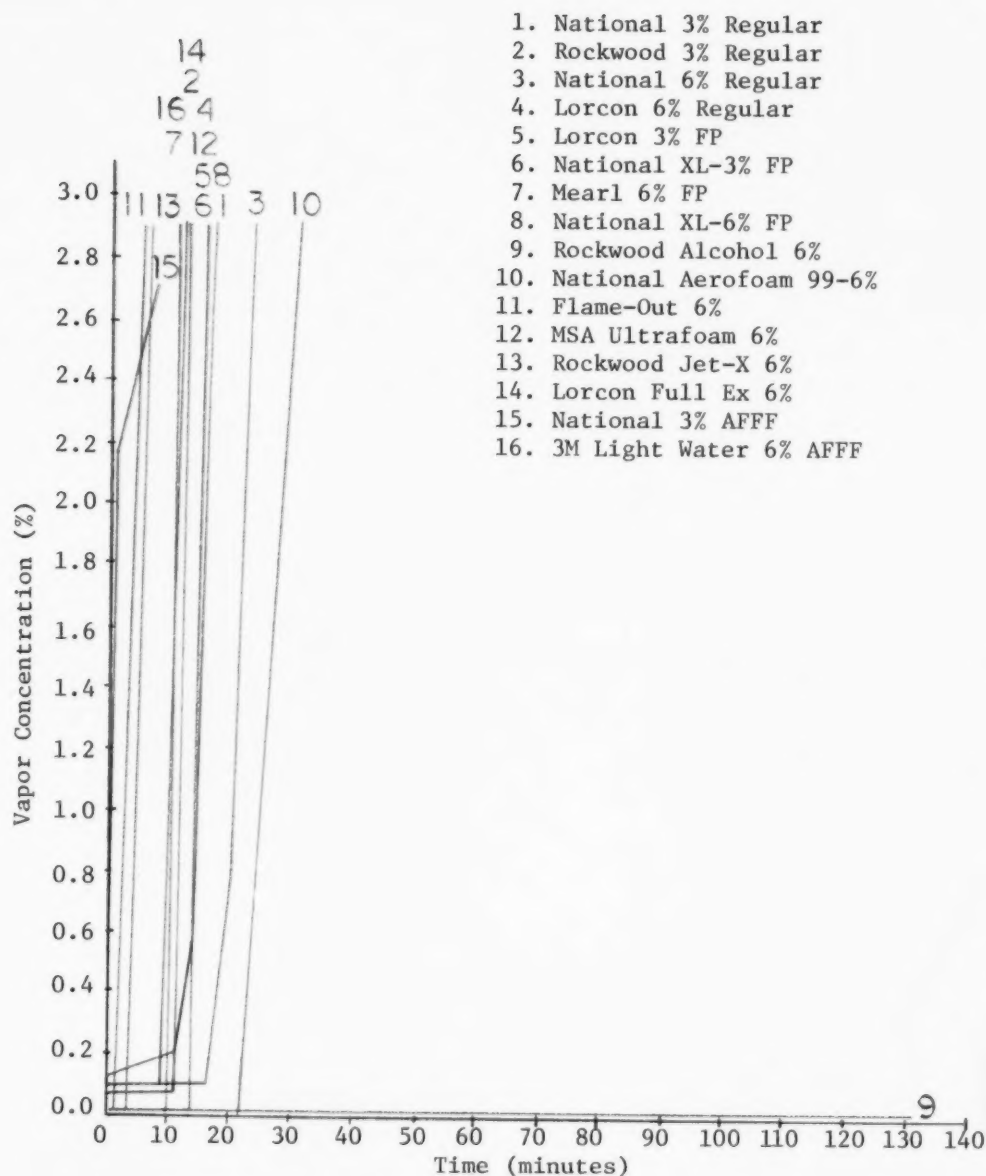


Figure 10. Ethyl ether with low expansion foams
 (initial foam height was 2 in.)

foams all have long mitigation times. In Figure 9, cyclohexane is the hydrocarbon tested with the various foams. The 6% surfactants again show the shortest mitigation times. The 3% and 6% AFFF's are intermediate and the remaining foams are all very effective in mitigating the vapors from cyclohexane. Figure 10 shows the foam agents with ethyl ether. Only the Rockwood 6% alcohol foam shows a long vapor mitigation time. The remaining foam agents have short mitigation times.

The data for the tests with the remaining volatile chemicals are given in Figure 11 through 15. Figure 11 gives the data for low expansion foams with toluene, Figures 12 through 15 give similar data for ethyl benzene, n-butyl acetate, triethylamine and n-octane, respectively.

The low expansion foams were resistant to collapse with all polar hydrocarbons except triethylamine. Only the fluoroprotein and Rockwood alcohol foams did not break down with triethylamine.

In general, the relative mitigation times of the low expansion foam categories are: 6% alcohol > 3% or 6% AFFF's > 6% surfactant. Of all the properties examined, drainage was determined to be the most important. In Figure 16, the rate of vapor release is plotted for a spill of benzene under essentially stag-nant conditions. Curve 1 is for a free spill. Curves 2 and 3 compare the effectiveness of two protein foams at the same expansion and cover thickness. Clearly Protein B is the superior material.

The only difference between protein foams A and B is drainage. The point is presented more clearly in Figure 17 where the thickness of foam A has been doubled in the respect to foam B and it is still not equivalent.

This feature was found to be true of all foam types. Figure 18 shows the vapor control capabilities of high expansion foam of two surfactant agents. Here also the slower draining foam provides the superior performance.

Laboratory test results for liquefied gases--The result of foam application on a liquefied gas appears to be dependent on the drainage characteristics of the foam. The water in the foam supplies heat to the liquefied gas in three possible ways: the latent heat of fusion as the water freezes, the heat capacity due to temperature changes and the heat of solution for water reactive chemicals. The heat input by water increases the evaporation rate. In many cases the heat input from the freezing water is greater than the heat of vaporization of the liquefied gas. A very low rate of water addition is desirable; this can best be accomplished by using a high expansion foam with a low drainage rate. However, high expansion foam (500:1) could not be tested in the laboratory due to the large quantity of liquefied gas needed for the high expansion foam tests. More specific information on the performance of high expansion foam had to await field testing. Only representative foams from the medium and low expansion categories were tested. The following foams were used in the laboratory liquefied gas study:

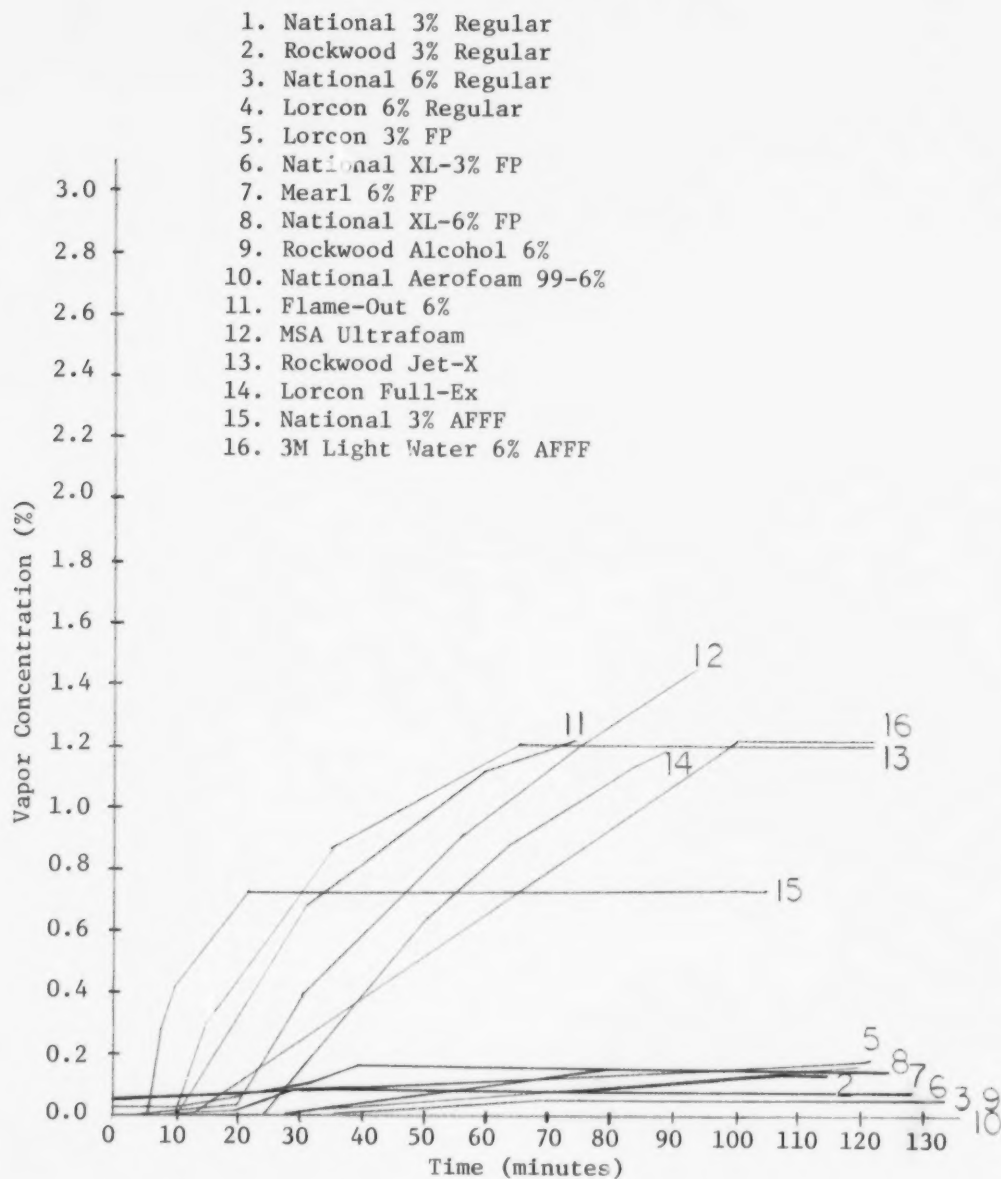


Figure 11. Toluene with low expansion foams
 (initial foam height was 2 in.)

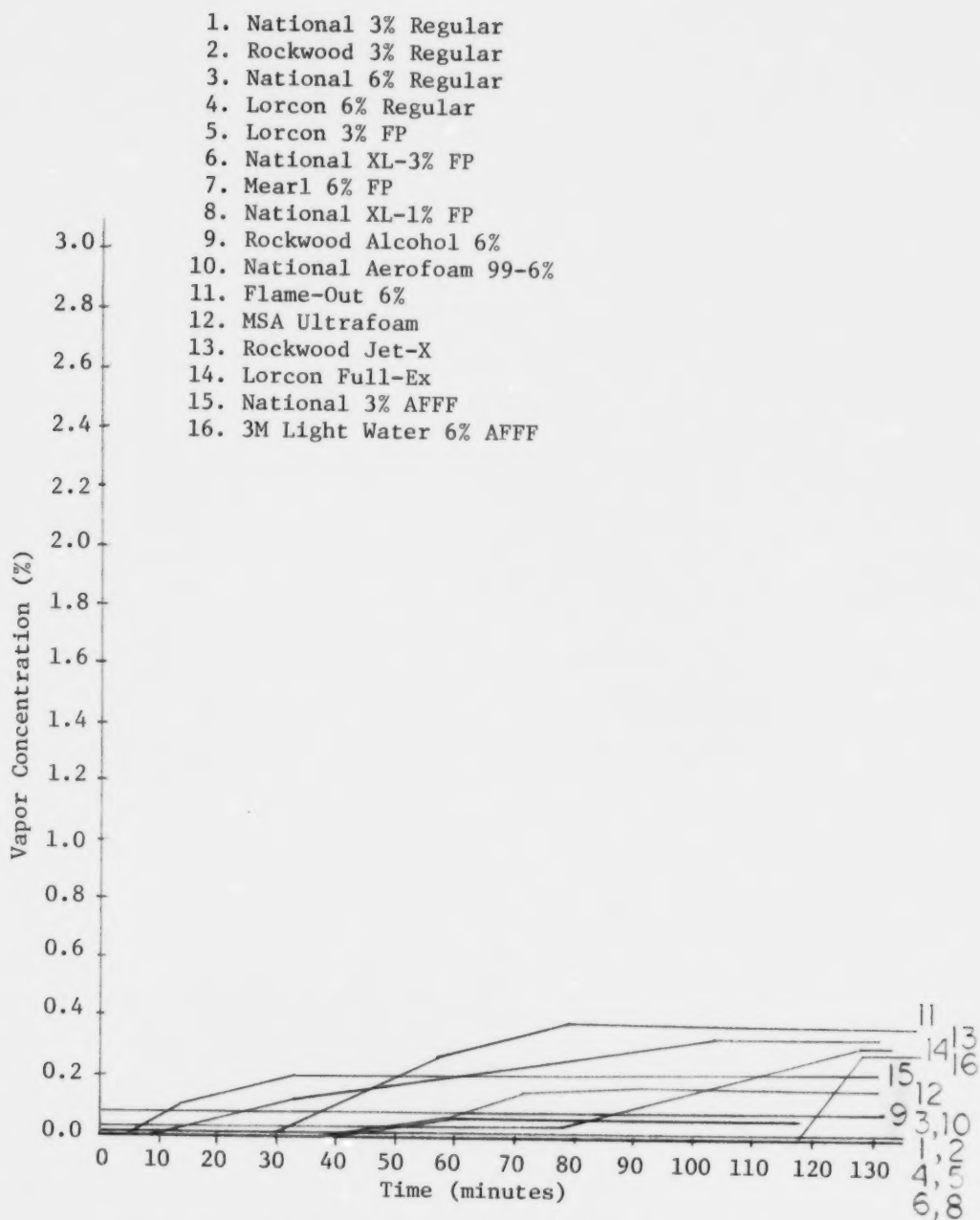


Figure 12. Ethyl benzene with low expansion foams
 (initial foam height was 2 in.)

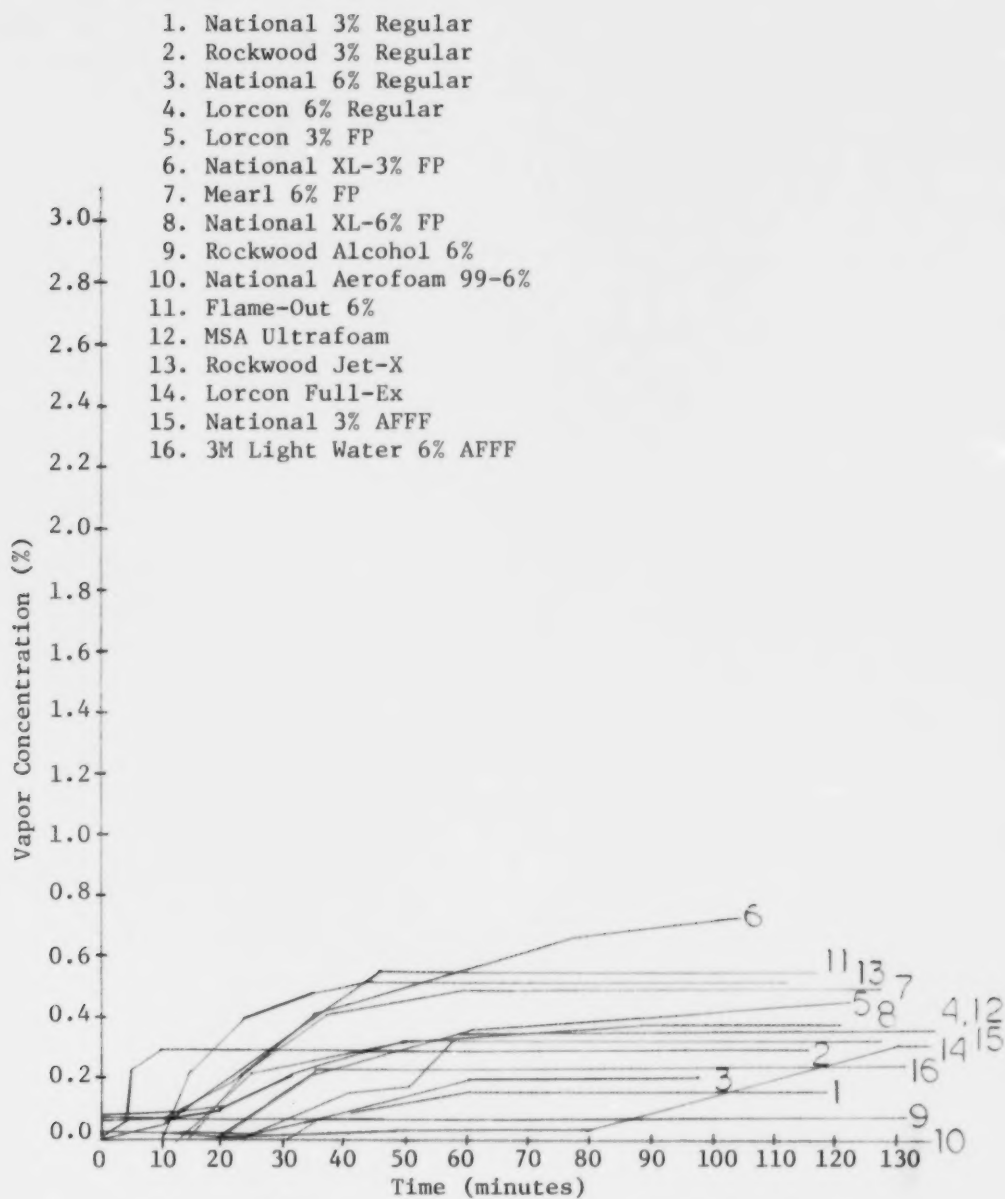


Figure 13. n-Butyl acetate with low expansion foams
 (initial foam height was 2 in.)

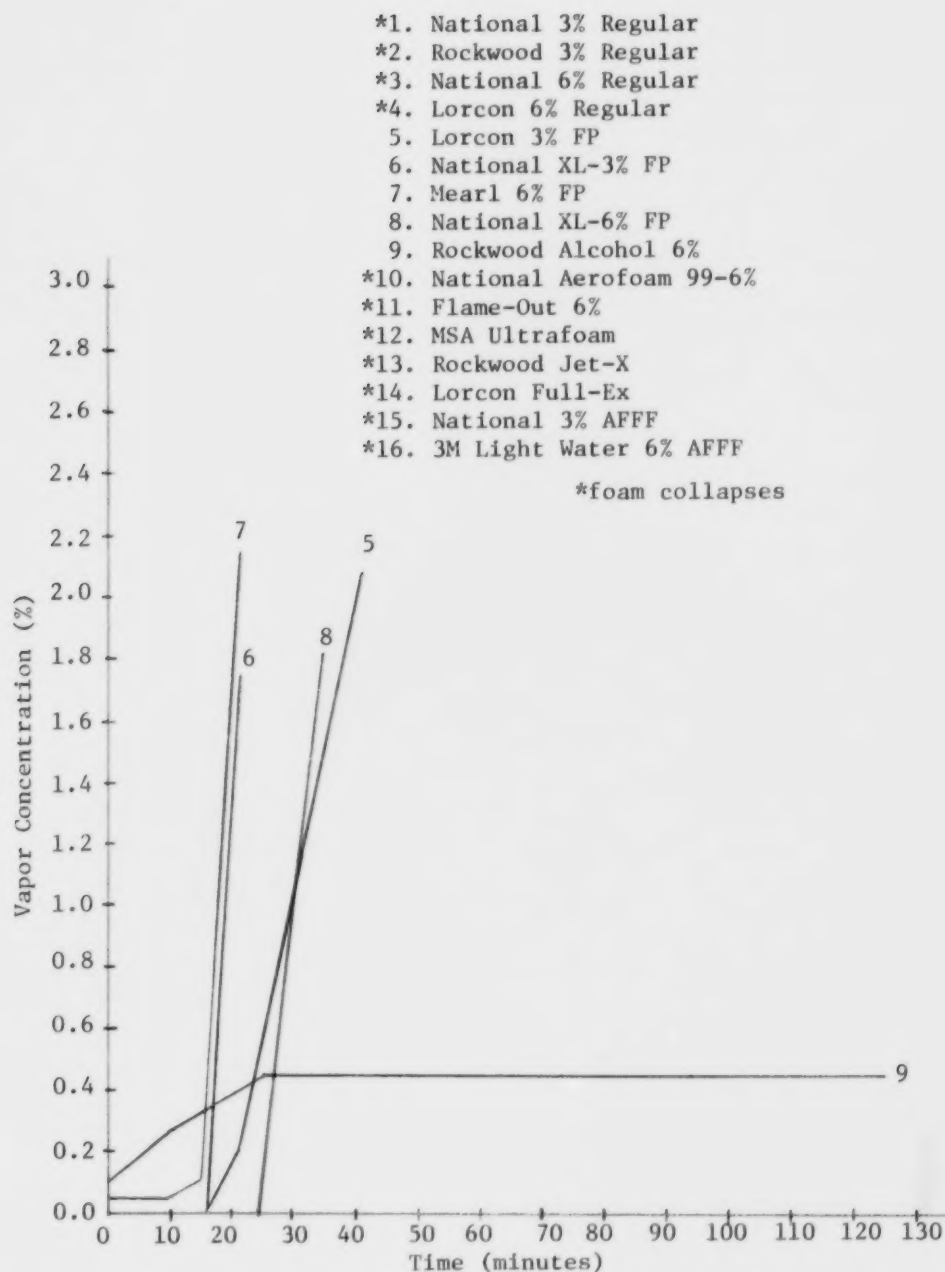


Figure 14. Triethylamine with low expansion foams
 (initial foam height was 2 in.)

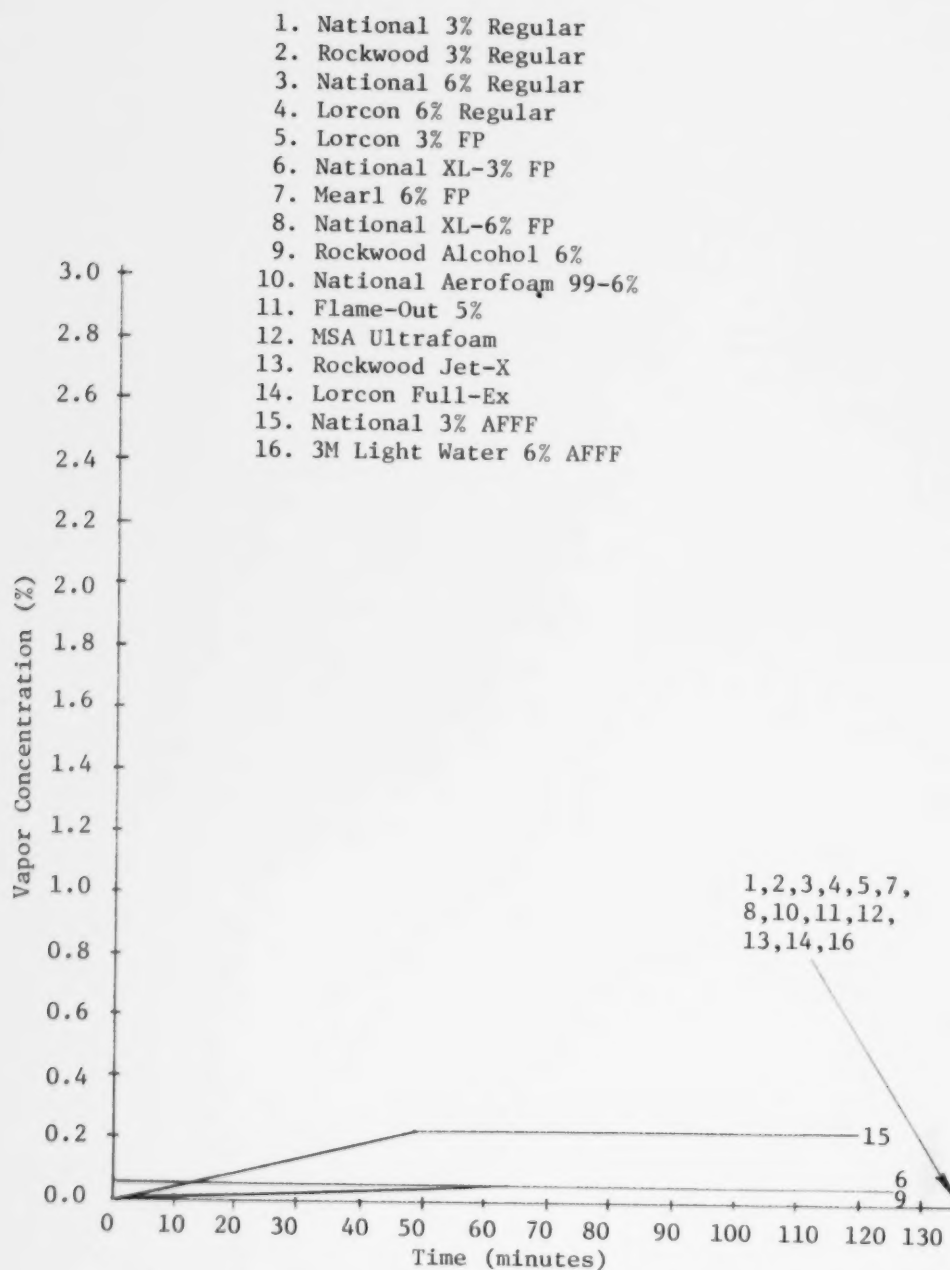


Figure 15. n-Octane with low expansion foams
(initial foam height was 2 in.)

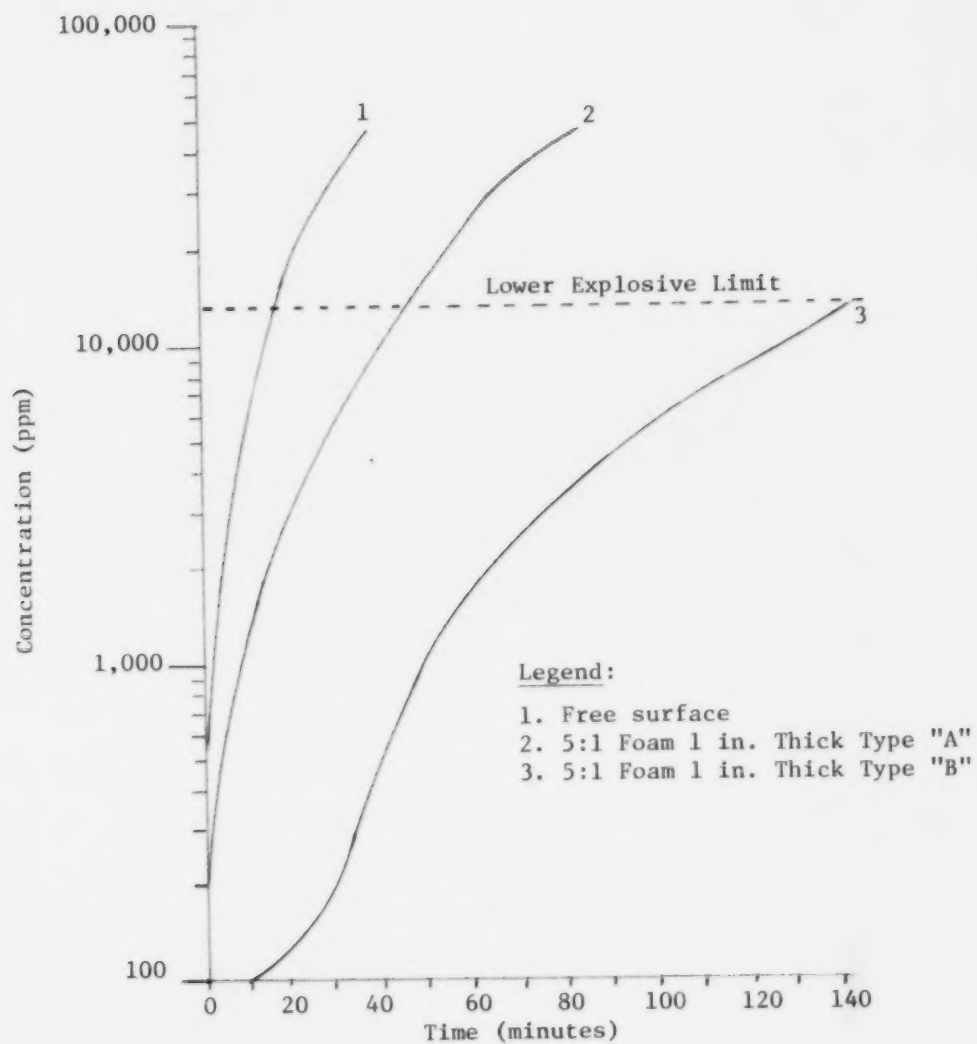


Figure 16. Vapor buildup over benzene surface comparing two types of protein foam

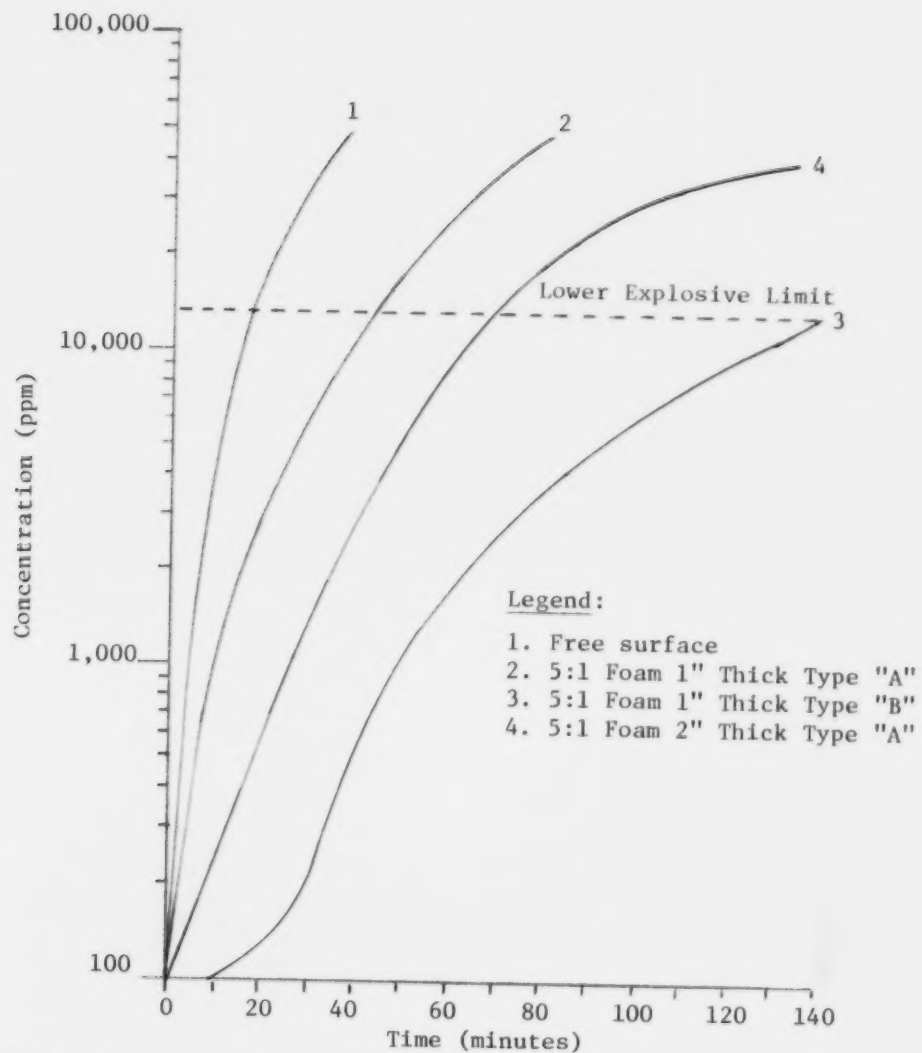


Figure 17. Effect of doubling foam "A" thickness for benzene spill of figure 16

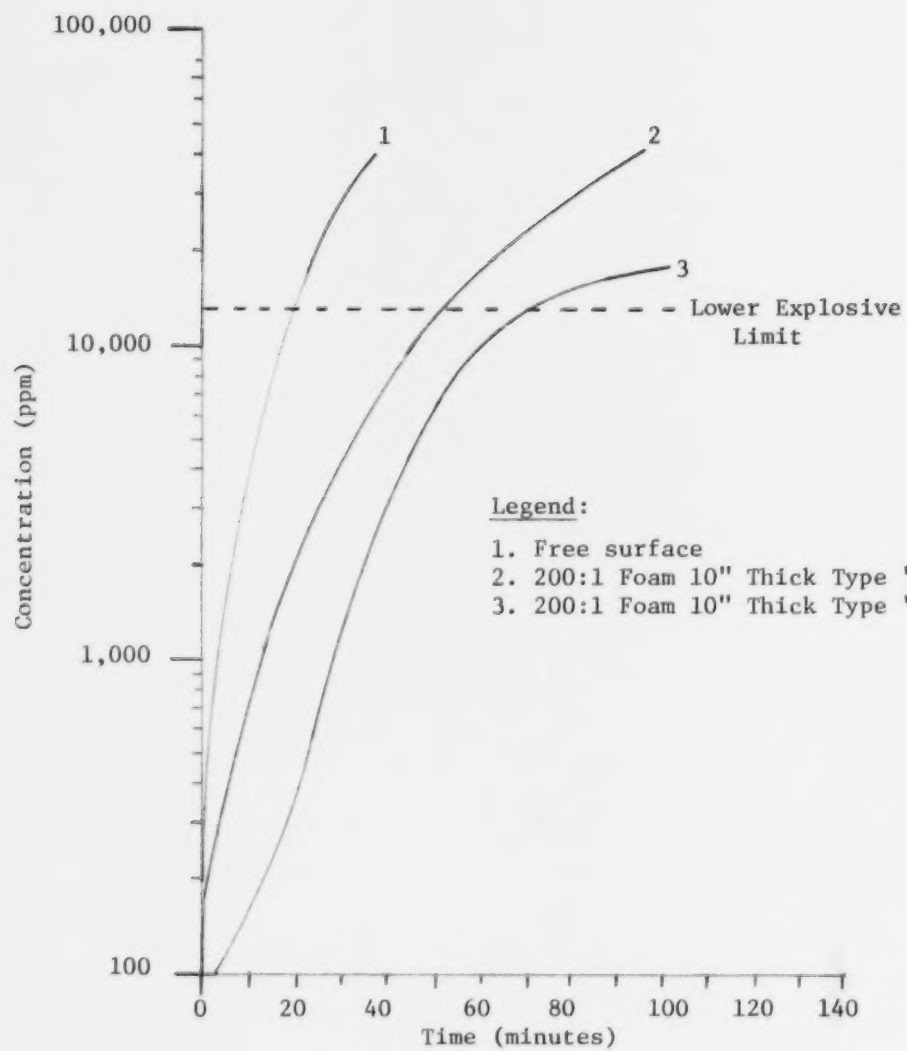


Figure 18. Vapor buildup of vapor concentration over benzene surfaces comparing two high expansion foams

Medium Expansion:	MSA Ultrafoam
	National AFFF 3%
	Emulsiflame
Protein:	National 6% Regular
Fluoroprotein:	National 3%
Alcohols:	National Aerofoam 99-6%
	Rockwood Alcohol 6%
Low Expansion	
Surfactants:	MSA Ultrafoam
Low Expansion AFFF:	National 3%

For liquefied ethylene the heat input by water is greater than the heat of vaporization. As soon as any foam system was applied to liquefied ethylene the boil off rate increased. Since the specific gravity of liquid ethylene is 0.569, any water draining from the foam became frozen and sank, exaggerating the boil off. Low expansion foams increased the vaporization rate more than the medium expansion foam because of their higher water content. Protein foams which were applied as a 5 cm cover also became frozen at the foam-liquid interface. Channels formed through the frozen foam layer, permitting the liquefied ethylene to evaporate. The remaining unfrozen foam layer frothed 2 to 3 times its original 5 cm thickness. permanent channels through which ethylene vapors continued to evaporate were formed even through the froth.

The low expansion surfactant and AFFF also frothed after application to 4 to 5 times their original thickness. Since the bubbles are filled with ethylene, the frothing is probably not beneficial. Medium expansion foams also exaggerated boil off but not as much as the low expansion foams. After application of a medium expansion foam cover, large bubbles of ethylene passed through the foam column due to an increased boiling rate. Wet medium expansion foams resealed themselves after the large bubbles passed through the foam column. As the foam drained and dried out the ethylene bubbles formed permanent channels as the walls froze.

Application of foams to liquefied propane produced about the same results as with ethylene, except the boil off was not as intense.

Liquefied 1,3-butadiene showed results similar to ethylene. The boil-off intensity due to foam application was less for the medium expansion foam than for low expansion foam.

Ethylene oxide, because of its higher boiling point, did not cause the water in the foams to freeze but the heat of solution was sufficient to exaggerate boil off upon foam application. Protein foams formed crevices in a short period of time due to foam degradation, exposing the liquid ethylene oxide-water solution. Of the protein based foam agents, only Rockwood alcohol foam formed a stable cover. The low expansion surfactant and AFFF foams formed stable covers after some initial frothing. Medium expansion foams all collapsed when generated onto the ethylene oxide surface.

Liquid ammonia has a high heat of solution, which along with the other heat inputs produced intense boiling upon foam application. Protein based

foams exaggerated the boil off more than the other types of foams. Rockwood alcohol foam was the only protein based foam that did not form a stable cover. It collapsed in several minutes. Low expansion surfactant and AFFF foams frothed to 4 times their original thickness but were stable. Medium expansion, in relation to the other foams, showed the smallest increase in the boil off rate. The medium expansion foams also frothed to 1.5 to 2 times their original height of 30 cm, but the collapse rates were normal.

Chlorine has a low heat of vaporization with limited water solubility. Even so, the heat input of water caused boil off to be intensified. Medium expansion foam collapsed in 5 minutes leaving only the frozen interface composed of ice and chlorine hydrate over the liquid surface. Protein foams thickened upon application. Chlorine bubbling through the foam produced a very porous cover. Alcohol foams were quickly destroyed by liquefied chlorine. The low expansion surfactant and AFFF foams frothed 7 to 8 times their original thickness and formed a relatively stable foam. The bubbles were filled with chlorine, however, and foam collapse released chlorine.

During all of the chlorine tests a green vapor cloud was clearly visible over the foam cover. Water has a lower density with respect to liquefied chlorine water. Drainage from the foam forms an ice cover over the liquefied chlorine, but the cover at the foam-liquid chlorine interface is porous and allow significant quantities of chlorine vapors to be released.

Hydrogen fluoride, because of its extremely high heat of solution, boiled and fumed violently upon application of foam. A medium expansion foam cover could not be developed until the hydrogen fluoride was somewhat diluted. Low expansion protein, surfactant and AFFF foams were stable over liquid HF but fuming continued above the foam cover. Alcohol foams were destroyed. Hydrogen fluoride vapor, because of its low specific gravity, may dissipate fairly readily without foam cover. Foam does not appear to help.

Sulfur trioxide produced more violent reaction than hydrogen fluoride when foam was applied. Medium expansion foams collapsed, with splattering and the release of black fumes. After dilution by continued application, medium expansion foams formed a short lived cover above the sulfur trioxide. All the low expansion foams also produced black fumes, intense splattering and boiling upon application but they eventually formed a relatively stable foam cover.

Matrix Revision

Upon completion of the laboratory test program, the data obtained was compiled and evaluated. Using this data, the matrix prepared in the beginning of this task was revised and annotated. The matrix is shown in Table 9.

TASK II - FIELD TESTING

The laboratory tests provided a basic definition of capabilities of the currently available foam systems to control spills of volatile hazardous chemicals.

TABLE 9. PRELIMINARY MATRIX OF FOAM CAPABILITIES
ON THE SPILLED HAZARDOUS CHEMICALS LISTED

		Recommend	1	2	3	4	5	6
Organics-Aliphatic Acids	- Acetic Acid	ND	ND	ND	ND	ND	ND	ND
	- Caproic Acid	ND	U	ND	ND	ND	ND	ND
Alcohols	- Amyl Alcohol	ND	U	U	ND	ND	ND	ND
	- Butanol	R	E-	E-	E-	E-	A+	E-
	- Butyl Cellosolve	ND	ND	ND	U	ND	ND	ND
	- Methanol	R	E-	E-	E-	E-	A+	E-
	- Octanol	R	U	U	U	U	U	ND
	- Propanol	R	E-	E-	E-	E-	A+	E-
Aldehydes & Ketones	- Acetone	R	E-	E-	E-	E-	A+	E-
	- Methyl Butyl Ketone	R	E-	E-	U	ND	A+	ND
	- Methyl Ethyl Ketone	R	U	U	U	ND	A+	ND
Esters	- Butyl Acetate	ND	U	U	U	U	ND	ND
	- Ethyl Acetate	ND	U	U	U	U	ND	ND
	- Methyl Acrylate	ND	U	U	ND	U	ND	ND
	- Methyl Methacrylate	ND	U	U	ND	U	ND	ND
	- Propyl Acetate	ND	U	U	U	U	ND	ND
Halogenated	- Butyl Bromide	ND	U	U	ND	ND	ND	ND
	- Methyl Bromide	ND	U	U	ND	ND	ND	ND
	- Tetrachloroethane	ND	U	U	ND	ND	ND	ND
Hydrocarbons	- Heptane	R	C+	B+	B+	B+	A+	C+
	- Hexane	R	C+	B+	B+	B+	A+	C+
	- Octane	R	C+	B+	B+	B+	A+	C+
Nitrogen Bearing	- Dimethyl Formamide	ND	U	E-	ND	ND	ND	ND
Organics-Aromatic Hydrocarbons	- Benzene	R	C+	B+	B+	B+	A+	C+
	- Tetrahydronaphthalene	R	U	U	U	ND	ND	U
	- Toluene	R	C+	B+	B+	B+	A+	C+
Organics-Alicyclics	- Cyclohexane	R	B+	A+	B+	B+	C+	C+
Organics-Industrial	- Gasoline	R	C+	B+	B+	B+	A+	C+
	- Kerosene	R	C+	B+	B+	B+	A+	C+
	- Naptha	R	C+	B+	B+	B+	A+	C+
	- Paint Thinner	R	C+	B+	B+	B+	A+	C+
Organics -Cryogens	- Liquefied Natural Gas	R	C-	A+	E-	E-	E-	E-
Inorganics	- Silicon Tetrachloride	R	E-	A+	E-	E-	E-	E-
	- Sulfur Trioxide	R	E-	A+	E-	E-	E-	E-
Inorganics-Cryogens	- Ammonia	R	C+	A+	C+	C+	E-	C+
	- Chlorine	R	C+	C+	C+	C+	E-	E-

IDENTIFICATION OF SYMBOLS

Type of Foam:	1	2	3	4	5	6
	Surfactant Low Ex	Surfactant High Ex	Protein	Fluoroprotein	Alcohol	AFFF
U	Limited data available - capabilities uncertain					
ND	No data					
R	Foam use recommended over spill					
A+	Best foam formulation					
B+	Next best foam formulation					
C+	Acceptable in some situations					
E-	Unsuitable foam formulation					

Based upon the results from the laboratory tests a selection was made of candidate materials for field testing. The selection excluded any chemical which has a high toxicity (low TLV). Thus, for instance, HF and SO₃ were not considered. Such exclusion did not hurt the verification of the laboratory data. Data from other materials were combined and translated to approximate the conditions these materials would present.

The foam agents chosen for a majority of the field tests were those from each foam class that had the best drainage characteristics, i.e., retained their water content. Several foam agents with poor drainage were field tested to substantiate the laboratory results.

Three separate field test sites were used. The first tests were conducted at the Evans City plant of MSAR. These tests were for the hazardous liquids such as benzene. The second site was a remote location near Norman, Oklahoma, where the liquefied gases such as propane were tested. To test chlorine and ethylene oxide, a very remote area with security was needed. Thus, the third test site was at the DOE facility at Mercury, Nevada.

Evans City Field Tests

The results of the field tests with volatile organics are shown in Table 10. These field tests were conducted at Evans City where 220 liters of hazardous chemical were placed into a 3 m by 3 m pan. Gas sensors were placed at 5 locations just above the foam cover to determine the length of time a particular foam reduced the vapors from the pan. For most of the low expansion foam tests, 75 liters of water were used to produce foam for each test. The foam thickness varied from 5.7 cm for the protein based foams to 10 cm for the surfactant foams. The Rockwood Alcohol foam, because of its thicker nature, used 115 liters of water to completely cover the solvent in the pan. The high expansion foams used less than 2 liters of water to provide a foam cover 30 to 45 cm in depth. The values shown in the table indicate the length of time for a significant vapor breakthrough (normally 1% vapor concentration). In most cases, once vapor breakthrough began the vapor concentration rose very rapidly above the foam cover.

The results in Table 10 are generally similar to the earlier laboratory tests if the foam agents are compared on a relative basis. The notable difference between the field and laboratory test results was the stability of the foams against polar compounds. In the laboratory the liquid volume ratio of foam solution to solvent was 4 to 1. The large amount of water from the foam solution diluted the polar solvents. In the field tests the ratio of foam solution to solvent was 1 to 2.75. The effect of water dilution was greatly reduced. No foam agent except Rockwood alcohol was resistant to collapse with the polar compounds which have a high ambient vapor pressure, acetone and ethylether. N-Butyl acetate (with a low vapor pressure) caused all the low expansion foams except fluoroprotein, alcohol, surfactant and fluorosurfactant foams to collapse.

Triethylamine is not included in the table because of large variations which occur in solubility around 20°C. This property of triethylamine results

TABLE 10. FOAM MITIGATION TIMES* -- TIME FOR SIGNIFICANT VAPOR BREAKTHROUGH

Foam Agent	Cyclohexane	Benzene	Toluene	Ethyl Ether	Acetone	n-Butyl Acetate	n-Octane	Triethylamine
National 6% Regular Protein	60	60	60	Collapsed	Collapsed	Collapsed	60	--
Lorcon 6% Regular Protein	--	30 ¹	--	"	"	--	--	--
Lorcon 3% Fluoroprotein	--	30 ¹	60	"	"	--	--	--
National XL-3 Fluoroprotein	60	30 ¹	--	"	"	60	--	--
Rockwood Alcohol	60	60	60	20	60	60	60	--
National Aer-O-Foam 99-6%	--	5	--	Collapsed	Collapsed	--	--	--
MSA Ultrafoam Low Expansion	60	15 ¹	55	"	"	25	--	--
Rockwood Jet-X Low Expansion	--	15	--	"	--	--	--	--
Lorcon Full-Ex Low Expansion	--	35	10 ¹	"	Collapsed	--	--	--
National 3% AFFF	60	13	60	15 ²	"	60	60	--
3M Light Water 6% AFFF	--	6	--	16 ²	"	--	--	--
Rockwood Jet-X High Expansion	--	12	--	Collapsed	Collapsed	--	--	--
Lorcon Full-Ex High Expansion	30	25	15 ¹	"	"	--	--	--
MSA Ultrafoam High Expansion	60	16	23 ¹	"	"	Collapsed	15 ¹	--
3M Light Water 6% AFFF High Expansion	--	11	--	--	--	--	--	--
National 3% AFFF High Expansion	--	10	--	--	--	--	--	--

*Time given in minutes

¹Significant wind damage

²Gap formed between the foam and solvent

in significantly different responses depending upon the ambient temperature, making a generalization difficult without further investigation.

N-Octane did not cause any of the foam agents to collapse.

For the nonpolar compounds shown in Table 10, all of the low expansion foam agents with low water drainage rates form an effective mitigation barrier when using the lower explosive limit as the point of measure. Foam agents with high water drainage rates showed poor results. The loss of water results in a light, easily permeated foam layer which quickly loses its ability to mitigate the vapor. In general, the protein based foam agents provide a longer mitigation time than the surfactant and fluorosurfactant based foam agents.

High expansion foams provide less protection time than low expansion foams, due primarily to wind effects. However, the high expansion foam can be applied much more rapidly and with about one-sixtieth of the liquid foam solution volume. Repeated applications of high expansion foams could provide the same mitigation time as low expansion foams with much less water.

Oklahoma Field Tests

Field testing of liquefied ethylene, propane, butadiene and ammonia was conducted at the test site of Energy Analysts in Norman, Oklahoma. The actual testing sequence is shown in Table 11.

In each test, a 3 m x 3 m concrete pit was filled with liquefied gas to a depth of 7.5 to 10 cm. Gas sensors were located downwind of the pit to measure the vapor concentration before and after foam application. Time was allowed for the liquefied gas placed into the pit to achieve steady state boil off. Foam was applied until the surface was covered. The foam depth was 5-8 cm for low expansion foam and 15 to 30 cm for medium and high expansion foam.

Additional tests were run with propane in the 3 m x 3 m pan to compare a medium vs low expansion surfactant (MSA Ultrafoam) and two regular protein foam agents (Rockwood and National). Because the odor was causing some concern to nearby inhabitants the final test with ammonia using the 6% Light Water AFFF was done in a smaller 1.5m x 1.5m pan.

The following data points were recorded on magnetic tape for computer analysis:

- wind speed - 2 locations
- wind direction - 2 locations
- wet bulb temperature - 2 locations
- dry bulb temperature - 2 locations
- relative humidity - 2 locations
- incident solar radiation - 1 location
- atmospheric pressure - 1 location
- downwind combustible vapor concentration - 10 locations
- downwind ammonia vapor concentration - 7 locations.

TABLE 11. TESTING SEQUENCE AT NORMAN, OKLAHOMA

<u>Liquefied Gas</u>	<u>Test Pan Size (meter)</u>	<u>Foam Agent</u>
Ethylene	3x3	MSA Ultrafoam (medium expansion)
"	3x3	6% Light Water AFFF
"	3x3	6% National Protein Regular
"		MSA Ultrafoam (high expansion)
Propane	3x3	MSA Ultrafoam (low expansion)
"	3x3	Rockwood Alcohol
"	3x3	6% National Protein Regular
"	3x3	6% Rockwood Regular Protein
"	3x3	6% Light Water AFFF
"	3x3	MSA Ultrafoam (medium expansion)
1,3-Butadiene	3x3	MSA Ultrafoam (medium expansion)
"	3x3	6% National Protein Regular
"	3x3	3% National Fluoroprotein
"	3x3	6% Light Water AFFF
Ammonia	3x3	MSA Ultrafoam (medium expansion)
"	3x3	6% National Protein Regular
"	1.5x1.5	6% Light Water AFFF

The data showed that the benefit of foam in mitigating the vapor hazard in terms of downwind gas concentration is a function of the gas density. The initial application of foam resulted in a sharp increase in the boil off rate. The magnitude of the increase varied inversely with the expansion of the foam and directly as a function of drainage -- the lower the expansion and/or the faster the drainage, the larger the magnitude of boil off pulse.

After the initial pulse, the boil off rate decreased as did the downwind gas concentrations, but not always below the values seen before foam application. For a spill of liquefied ethylene, where the vapor density at ambient conditions is equal to air, medium and high expansion surfactant foams afforded reductions in the downwind vapor concentration. This reduction was in the range of 10%. With low expansion foams, protein-based or AFFF, the downwind vapor concentration persisted at a level greater than that from a free spill. It was noted that with ethylene, even under the best conditions the downwind gas concentration remained above the LEL for a considerable distance from the spill center.

The results for propane, where the vapor density is greater than air, followed closely those for ethylene, except the initial vapor cloud given off during foam application is smaller than in the case of ethylene. The propane vapor cloud tended to remain close to the ground. A medium surfactant and low expansion AFFF, protein, alcohol, and surfactant foams were tested. High expansion foam was not tested with propane. The medium expansion foam did not cause as large a vapor cloud as compared to low expansion when applied to a liquefied propane spill. No distinct change in the downwind concentration was distinguished with any of the foams after passage of the initial pulse.

Butadiene, whose vapor density is greater than propane, showed no reduction in the downwind vapor concentration when a foam cover of medium expansion surfactant, low expansion protein, AFFF or fluoroprotein was applied. This cloud remained closer to the ground than propane and appeared to take longer to dissipate.

In summary, for the gases ethylene, propane and butadiene the test results showed the influence of foam on downwind gas concentrations to be essentially controlled by gas density. The existing data on liquefied natural gas agree with this observation. The foam blanket acts as a heat sink for the liberated gas, warming it as it rises through the blanket. With LNG, which is considerably lighter than air at ambient temperatures, the effect of foam is pronounced. With ethylene, whose density is less than air at ambient temperatures, there is a small positive effect. Propane and butadiene, which are heavier than air, show no benefit from the warming action of the foam. The exaggeration of the boil off rate by the water draining from the foam may actually elevate downwind concentrations above that existing with a free spill. This behavior should carry over to other similar liquefied gases.

Changes in downwind gas concentrations are not the only consideration in assessing the ability of foam to control the vapor hazard of volatile chemicals. Benefits in controlling fires are also possible. Fire control was by definition beyond the scope of this contract. However, the most practical

method of dissipating residual spill material after completion of the vapor dispersion measurements was to burn it off. Observations made during these actions showed that in all cases the burn back (rate of fire spread) across the spill surface was considerably slower with a foam blanket in place than for a free liquid surface (Brown, 1979).

Ammonia showed a significant reduction in the downwind vapor concentration with the use of medium expansion surfactant foam, with the foam layer lasting for approximately 10 minutes. Until the foam began to break up, the vapor concentration remained below the vapor concentration before the application of the foam. The low expansion foams caused large vapor clouds to be given off upon application and no significant reduction occurred in the downwind vapor concentration after the vapor initial pulse dissipated. The protein foam formed channels through which ammonia continued to vaporize. The AFFF produced a great deal of frothing and bubbling. The success of the medium expansion foam in mitigating the ammonia vapors was probably due to the low water content and foam depth which facilitated scrubbing of the water reactive ammonia vapors. The only problem with the use of a medium expansion surfactant foam on an ammonia spill was the need for periodic make-up.

It is interesting to note that little or no ice was formed when the foam was applied to the ammonia spill. This is due, apparently, to a combination of solubility and heat of solution. In the cases of ethylene, propane and butadiene, a porous ice layer did form on the surface of the liquefied gas.

The results for ammonia are shown in Figure 19. The test conditions were as follows:

Low expansion (8:1) protein foam:

Pool size	3 m x 3 m
Foam depth	10 cm
Sensor #1	1.16 m from pool edge, 0.62 m elevation
Sensor #2	3.87 m from pool edge, 0.62 m elevation

Low expansion (8:1) AFFF:

Pool size	1.5 m x 1.5 m
Foam depth	10 cm
Sensor #1	0.7 m from pool edge, 0.62 m elevation
Sensor #2	2.94 m from pool edge, 0.64 m elevation

Medium expansion (250:1) surfactant foam:

Pool size	3 m x 3 m
Foam depth	30 cm
Sensor #1	1.24 m from pool edge, 0.62 m elevation
Sensor #2	3.1 m from pool edge, 0.62 m elevation

Data averaged for wind direction
but not for velocity or temperature

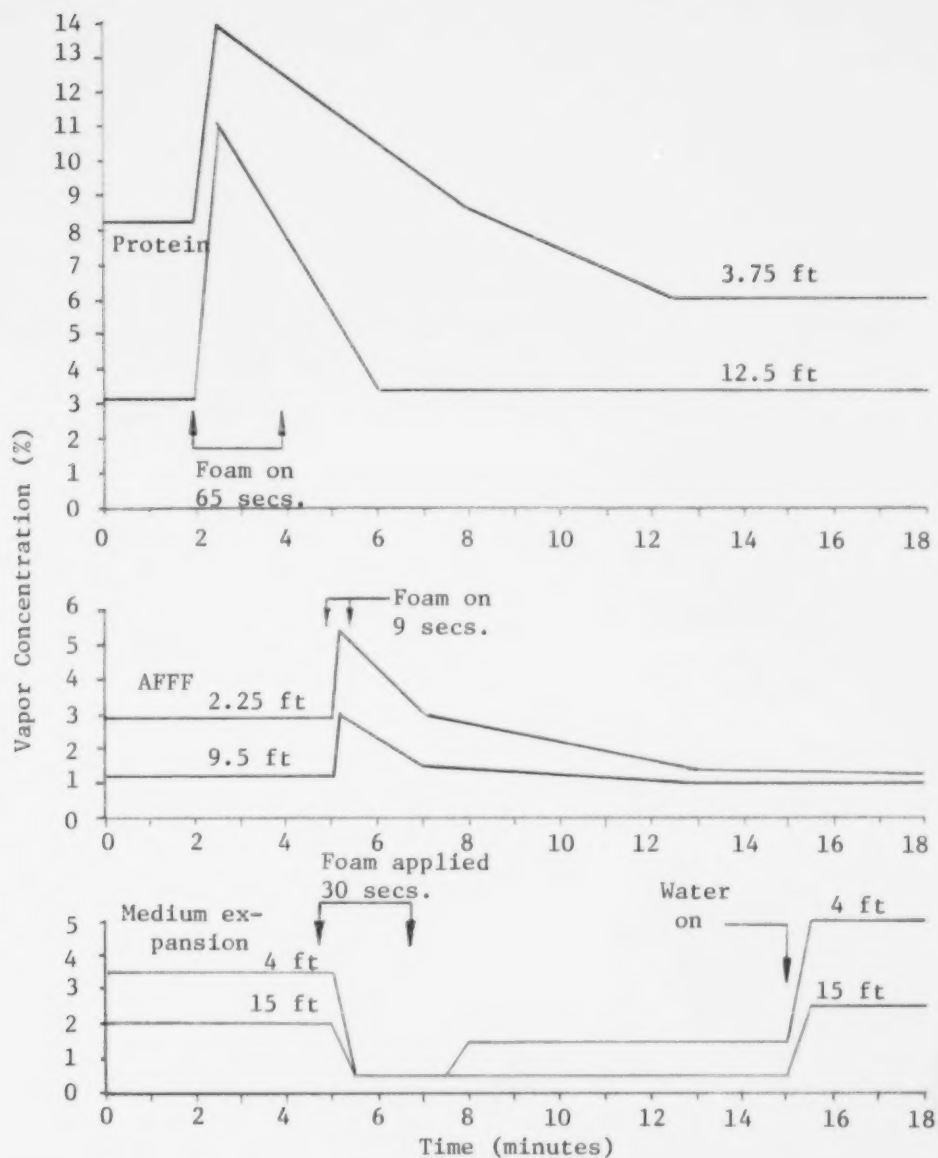


Figure 19. Effect of foam additions to anhydrous ammonia spills on downwind vapor concentrations

Protein foam showed no benefit and aggravates the situation upon initial application. Chimneys or voids formed in the blanket through which the gas was continuously released.

Due to the boiling action, no aqueous film was formed with the AFFF and the foam layer was strongly agitated by the gas release.

At the end of the medium expansion foam test, water was added to the spill. The chart readings show the dramatic increase in the downwind ammonia vapor concentration which occurred. The effects of water dilution alone should reduce the downwind vapor concentration. However, the heat of solution results in a higher vaporization rate which offsets the dilution effects. High expansion foam behaved similarly to medium expansion except that it degrades faster and showed somewhat less efficiency in controlling vapor release.

The reduction in the downwind vapor concentration after the application of a medium expansion surfactant foam is evident. In the test using the AFFF, the wind was shifting direction rapidly and large changes occurred in the sensor output. However, it is still evident that little reduction in the downwind vapor concentration was found.

Nevada Field Tests

At the Nevada test site, foam tests with liquefied chlorine were initially conducted using a weighed, insulated 0.93 m by 1.24 m pan to determine the chlorine weight loss before and after foam application. After the pan was filled to approximately 7.5 cm in depth with liquefied chlorine, the foam was applied. The amount of foam agent and water was also measured to establish a chlorine weight loss during and shortly after foam application. In the past, chlorine weight loss data was only noted before and after foam application. The weight of foam agent and water applied to the pan was not measured, and no weight loss could be determined as the foam was applied. It was certain that some chlorine was vaporized due to freezing of the foam.

Chlorine detectors were used to measure the downwind vapor concentration. However, the wind direction during the tests varied so widely that the vapor concentration data was not meaningful.

The results from the first foam tests are shown in Figure 20. High expansion surfactant foam (300:1) was used. Several minutes after application the high expansion foam collapsed. Note the increase in the chlorine vaporization rate after the first foam application. This increase is due to the heat of fusion of the water which drains from the collapsing foam. The water freezes in contact with the liquefied chlorine (-33°C) to form a porous ice layer which remain after the foam collapses. A second foam application did not produce the large increase in vaporization. However, this foam cover lasted only slightly longer than the initial foam cover.

In Figure 21 the results of a fluoroprotein foam application to liquefied chlorine are shown. The vaporization rate increased rapidly as the foam was applied and for sometime thereafter. There was some problem in determining

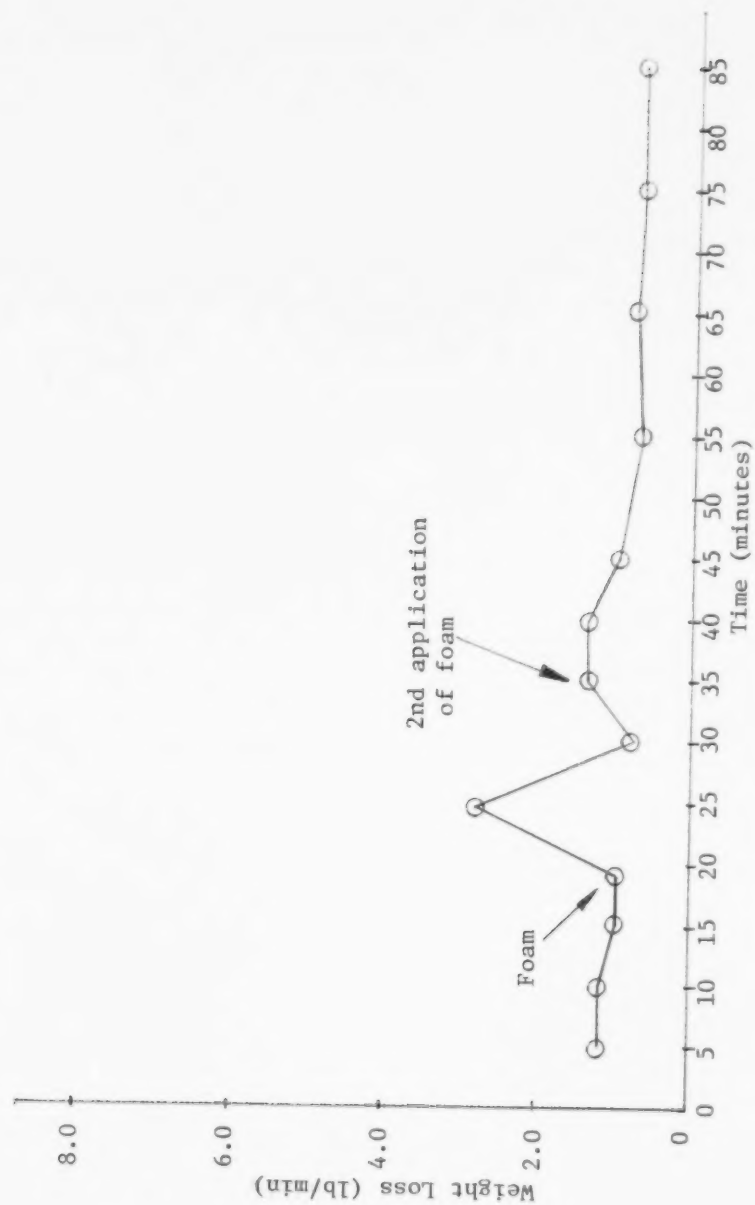


Figure 20. High expansion foam on liquefied chlorine

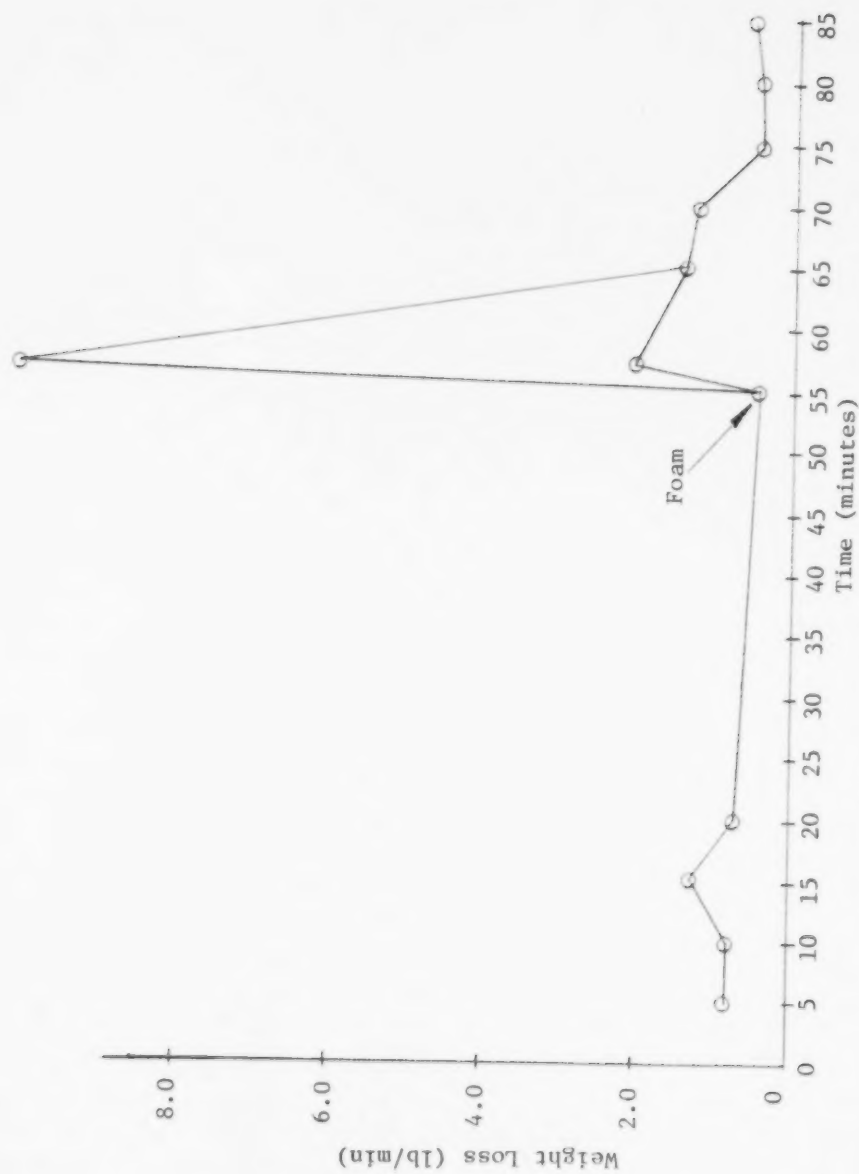


Figure 21. Fluoroprotein foam on liquefied chlorine

the volume of water added, so the possible lower and upper weight losses are shown. The actual weight loss was most likely near the upper limit because large chlorine vapor clouds were generated during foam application. The fluoroprotein foam thickened several minutes after application and a stiff, porous foam layer overlying an ice cover resulted. Beneath the ice layer there were several inches of liquefied chlorine. The volume of water needed to apply the low expansion fluoroprotein foam was much greater than the high expansion foam. The large quantity of water draining from the fluoroprotein foam produced the resultant increase in the vaporization of liquefied chlorine.

In Figure 22 the results for an aqueous film forming foam are shown. The gap between 30 and 50 minutes is due to difficulties with the foam generator. The difficulty was overcome and no further problems were experienced during the AFFF test. A increase in chlorine vaporization was also noted as the AFFF was applied to the liquefied chlorine surface. The AFFF collapsed several minutes after application and only a porous ice layer remained on the liquefied chlorine surface.

The problem with foam application to liquefied chlorine is primarily the water draining from the foam. The water content of the low expansion AFFF and fluoroprotein foams is approximately 1 liter of water per 8 liters of foam. With quarter drainage times of 1 to 2 minutes, assuming no abnormal collapse, the low expansion foams have lost 25% of their water content soon after application. The high expansion foam contains 0.016 liters of water per 8 liters of foam. Assuming no abnormal collapse and a quarter drainage time of 10 minutes, the high expansion foam would be a more desirable cover when water is a problem.

Since the high expansion foam appeared to produce the smallest increase in vaporization, it was then used in a larger test. A pan, 3 m by 3 m in size, was filled to a depth of approximately 5 cm with liquefied chlorine. The chlorine vaporization rate was calculated using depth measurements. A high expansion foam cover was applied and the change in depth was noted. The high expansion foams, as in the earlier case, collapsed shortly after application with the resultant increase in vaporization. The results for the 3 m by 3 m pan are shown in Figure 23.

All of the foams tested against a liquefied chlorine spill react with chlorine resulting in rapid degradation of the foam. The foam drainage, coupled with the rapid collapse, resulted in exaggerated boil off of the chlorine and a sharp increase in the downwind vapor concentration. Once an ice layer was established, successive foam applications were not as severe in exaggerating boil off.

This data does not show foam to provide any benefit in reducing the vapor hazard from a chlorine spill. It reflects the capability of those foam systems currently available to the fire service. The fact that successive foam applications do not create a large gas release pulse would indicate that foams which would be resistant to collapse upon contact with chlorine would be successful in reducing the vapor release rate. Since foams are known which are resistant to hydrochloric acid, development of a foam which is stable on chlorine should be possible.

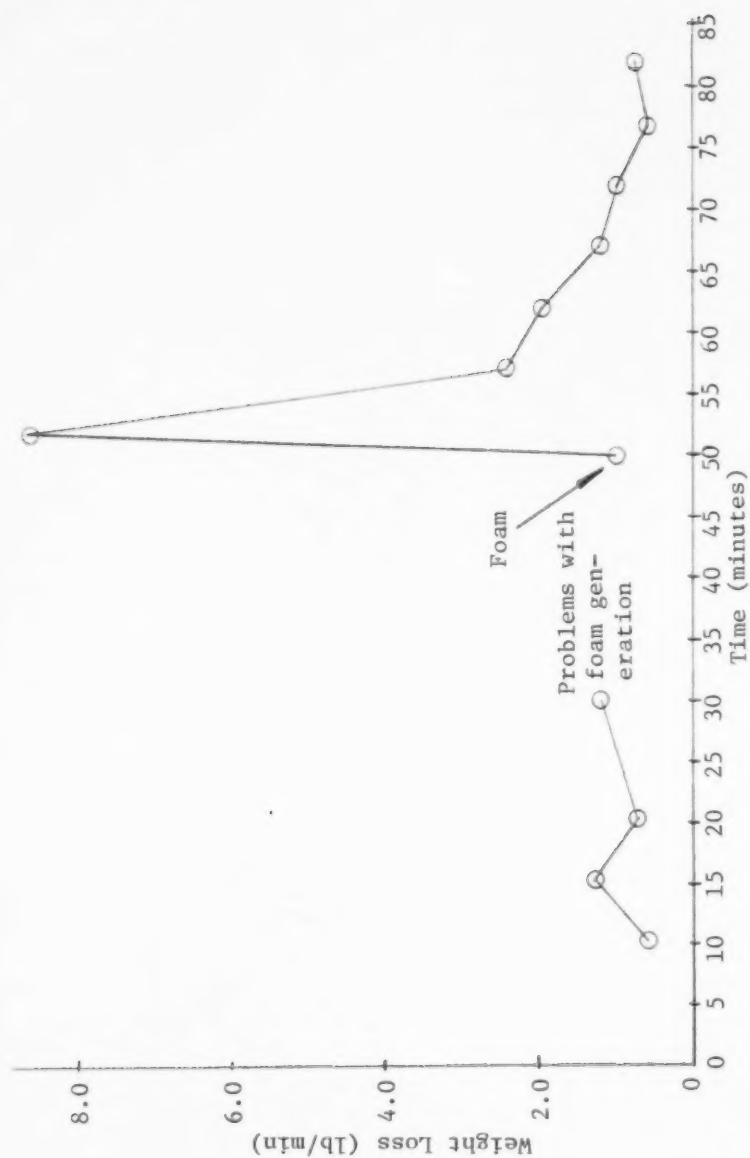


Figure 22. AFF on liquefied chlorine

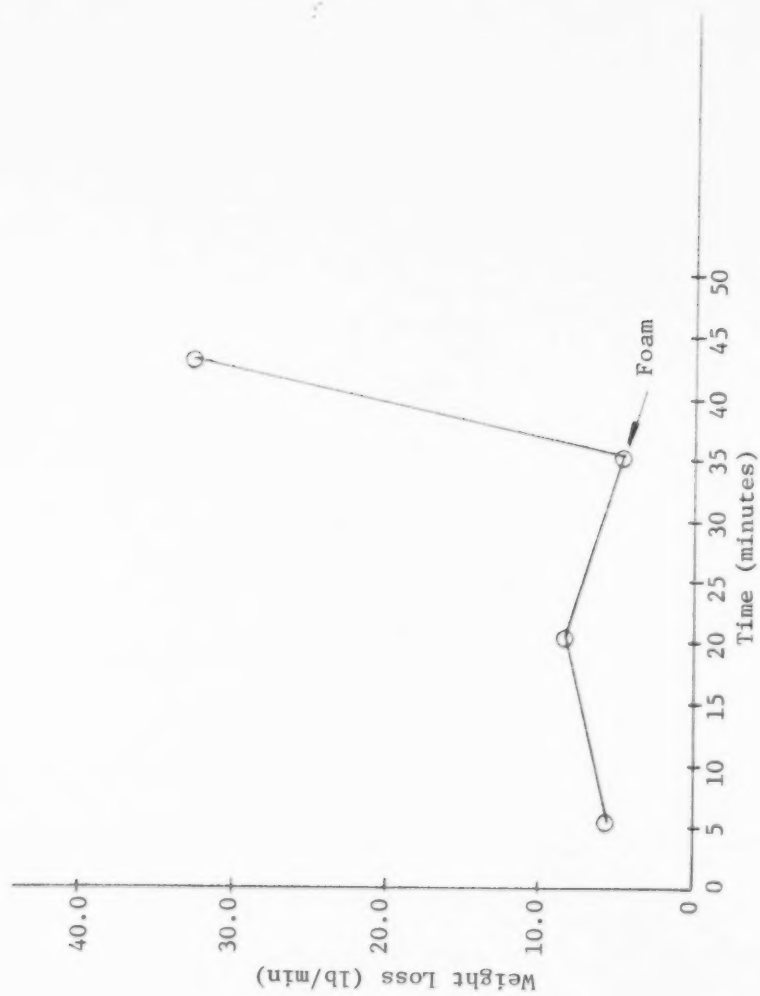


Figure 23. High expansion foam on liquefied chlorine

The ethylene oxide test was done in a 0.9 m x 1.2 m pan. After a 5 cm layer of liquefied ethylene oxide was established in the pan a foam cover was applied. Combustion gas sensors were used to determine the vapor concentration before, during and after foam application. The sensors were located over the downwind side of the pan, 30 cm from the ethylene oxide surface. Since the polar ethylene oxide causes all but alcohol based foams to collapse, only one mitigation test was conducted using the alcohol foam which had shown the properties in the laboratory (Rockwood Alcohol). The results of the alcohol based foam application are shown in Figure 24. Immediately upon addition of the alcohol foam, the vapor concentration of ethylene oxide increased rapidly to a level above the LEL. This result is probably due to the displacement of ethylene oxide vapors above its liquid by the foam. After the foam application was ended the vapor concentration decreased to approximately 30-40% of its uncovered value. Some of the reduction in ethylene oxide vapor concentration may be due to dilution by the water from the foam. After approximately 15 minutes, the foam cover was broken beneath one of the sensors to determine the vapor concentration of the uncovered ethylene oxide-water mixture. The vapor concentration increased from 25% to 60% showing that foam was effective in mitigating the vapors.

Foam Matrix

From these field tests a matrix has been established for the application of foam for use by first-on-the-scene personnel. This matrix is shown in Table 12. It provides a guideline for use of foam on a hazardous spill. The matrix shows that for polar compounds only a high quality alcohol foam is recommended for vapor mitigation. Even though other classes of foam agents may be stable against polar liquids with low ambient vapor pressures, it is difficult in a general matrix to include such exceptions.

For nonpolar liquids, a high quality low or high expansion foam could be used. Alcohol foams are not always the best foam agent to use if another class of foam is suitable. Alcohol foams do not flow as well as other types and therefore it would take longer to blanket a spill. If the addition of large volumes of water will further compound the problems of the hazardous spill, high expansion foam is recommended.

Liquefied gases were not included in the matrix because of the potentially harmful results if foam is used incorrectly. Given the very specific behavior of foams with liquefied gases, its use is recommended at this time only for gases whose vapor density at ambient temperatures is less than air at the same temperature.

TASK III - NOVEL FOAM SYSTEM

At the conclusion of Tasks I and II, additional foam agents were examined for their mitigation potential. These foams are available commercially but not in universal use by the five services.

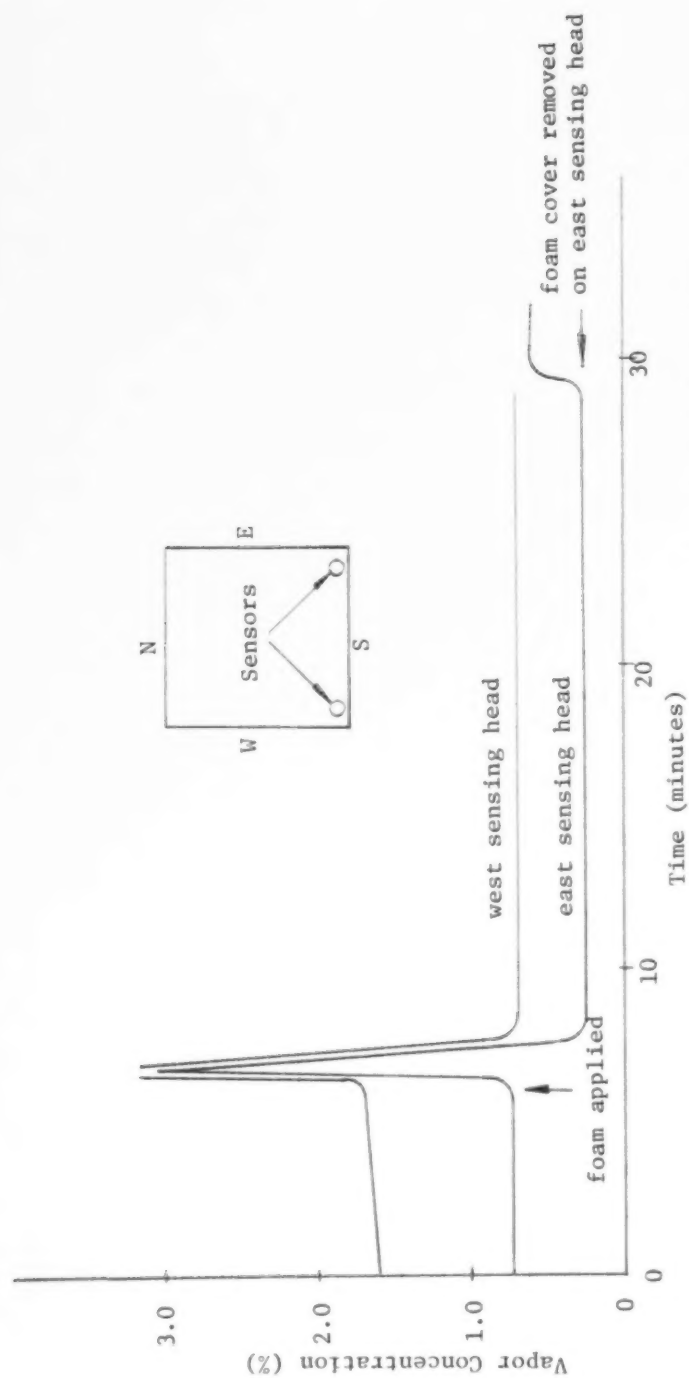


Figure 24. Ethylene oxide vapor concentration during alcohol foam test
(3 ft x 4 ft pan)

TABLE 12. MATRIX FOR POLAR AND NONPOLAR LIQUID HYDROCARBONS

	<u>Protein</u>	<u>Fluoroprotein</u>	<u>Alcohol</u>	<u>Surfactant</u>	<u>AFFF</u>	<u>Surfactant High Exp.</u>
Esters	E	E	A	E	E	E
Alcohols	E	E	A	E	E	E
Ethers	E	E	A	E	E	E
Aldehydes	E	E	A	E	E	E
Ketones	E	E	A	E	E	E
Phenols	E	E	A	E	E	E
Halogenated Compounds	A	A	C(b)	C(c)	C(c)	A(a)
Alkanes	A	A	C(b)	C	C	A(a)
Alkenes	A	A	C	C	C	A(a)
Alkynes	A	A	C	C	C	A(a)
Dienes	A	A	C	C	C	A(a)
Cycloaliphatic	A	A	C	C	C	A(a)
Aromatic	A	A	C	C	C	A(a)

(a) If wind speed <15 mph; also minimizes amount of water

(b) Only satisfactory because does not flow over spill as well as other types of foam.

(c) Foam drainage and mitigation times are not as good as protein based foams

A - Recommended

C - Satisfactory

E - Not Recommended

1. 3M Light Water Alcohol
2. National Universal Foam Liquid
3. National PSL Foam Liquid
4. MSA Long Life Foam

These foam agents were tested in the laboratory. The laboratory tests were similar to those used in Task I. The exception was the amount of volatile liquid used in the test and only low expansions were evaluated. A comparison was made with Rockwood All-Purpose Alcohol foam since it had shown the best mitigation potential for both polar and nonpolar compounds.

The volatile chemicals used to test the novel foam systems as well as the test results are, shown in Table 13.

TABLE 13 - TEST RESULTS FOR NOVEL FOAM AGENTS
(minutes to reach 50% of the LEL)

	<u>Rockwood</u>	<u>3M</u>	<u>National</u>	<u>MSA</u>
Benzene	90	90	90	90
Cyclohexane	90	90	90	90
Acetone	90	30	80	Collapse
Ethyl Ether	90	16	36	Collapse

The four chemicals are representative of the materials which during Task I seemed to provide a reliable indication of the foam behavior on a variety of chemicals.

The results show that for nonpolar compounds the novel foam agents perform as well as Rockwood Alcohol. However other conventional protein and fluoroprotein foam agents from Task I also performed well against nonpolar compounds. The real difference in performance between the novel foam agents and Rockwood is seen in the polar compounds. None of the novel foam agents were as effective against acetone nor ethyl ether as the Rockwood Alcohol foam. The 3M and National foam agents were stable against polar compounds, but the MSA Long Life Foam collapsed. The results show that these foam agents are not as effective as Rockwood All-Purpose foam against polar compounds. Nor do they provide any improvement over the widely distributed protein and fluoroprotein foam agents against nonpolar compounds.

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